



=> fil reg

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 jan.delaval@uspto.gov

STRUCTURE FILE UPDATES: 11 MAY 2003 HIGHEST RN 514167-89-6  
 DICTIONARY FILE UPDATES: 11 MAY 2003 HIGHEST RN 514167-89-6

TSCA INFORMATION NOW CURRENT THROUGH JANUARY 6, 2003

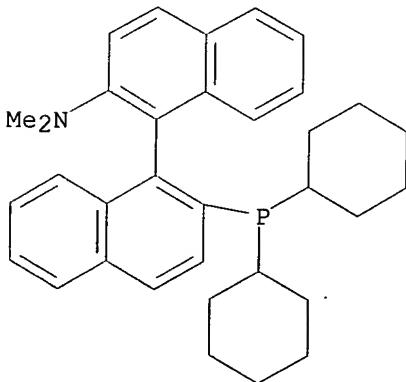
Please note that search-term pricing does apply when  
 conducting SmartSELECT searches.

Crossover limits have been increased. See HELP CROSSOVER for details.

Experimental and calculated property data are now available. See HELP PROPERTIES for more information. See STNote 27, Searching Properties in the CAS Registry File, for complete details:  
<http://www.cas.org/ONLINE/STN/STNOTES/stnotes27.pdf>

=> d ide can tot 111

L11 ANSWER 1 OF 3 REGISTRY COPYRIGHT 2003 ACS  
 RN 255882-16-7 REGISTRY  
 CN [1,1'-Binaphthalen]-2-amine, 2'-(dicyclohexylphosphino)-N,N-dimethyl-,  
 (S)- (9CI) (CA INDEX NAME)  
 OTHER NAMES:  
 CN (S)-(+)-2'-(Dicyclohexylphosphino)-N,N-dimethyl[1,1'-binaphthalen]-2-amine  
 MF C34 H40 N P  
 SR CA  
 LC STN Files: CA, CAPLUS, CASREACT, USPATFULL



\*\*PROPERTY DATA AVAILABLE IN THE 'PROP' FORMAT\*\*

4 REFERENCES IN FILE CA (1957 TO DATE)  
 4 REFERENCES IN FILE CAPLUS (1957 TO DATE)

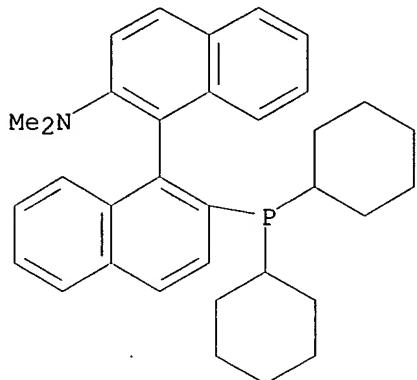
REFERENCE 1: 136:279128

REFERENCE 2: 135:107072

REFERENCE 3: 134:115733

REFERENCE 4: 132:108101

L11 ANSWER 2 OF 3 REGISTRY COPYRIGHT 2003 ACS  
RN 255882-15-6 REGISTRY  
CN [1,1'-Binaphthalen]-2-amine, 2'-(dicyclohexylphosphino)-N,N-dimethyl-,  
(R)- (9CI) (CA INDEX NAME)  
MF C34 H40 N P  
SR CA  
LC STN Files: CA, CAPLUS, CASREACT, USPATFULL



\*\*PROPERTY DATA AVAILABLE IN THE 'PROP' FORMAT\*\*

4 REFERENCES IN FILE CA (1957 TO DATE)  
4 REFERENCES IN FILE CAPLUS (1957 TO DATE)

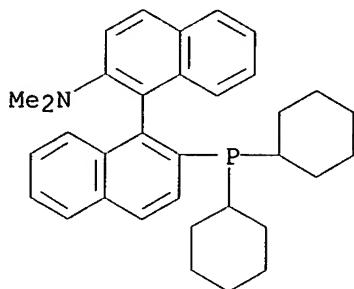
REFERENCE 1: 138:221639

REFERENCE 2: 136:309970

REFERENCE 3: 135:107072

REFERENCE 4: 132:108101

L11 ANSWER 3 OF 3 REGISTRY COPYRIGHT 2003 ACS  
RN 255835-81-5 REGISTRY  
CN [1,1'-Binaphthalen]-2-amine, 2'-(dicyclohexylphosphino)-N,N-dimethyl-  
(9CI) (CA INDEX NAME)  
FS 3D CONCORD  
MF C34 H40 N P  
SR CA  
LC STN Files: CA, CAPLUS, CASREACT, USPATFULL



\*\*PROPERTY DATA AVAILABLE IN THE 'PROP' FORMAT\*\*

3 REFERENCES IN FILE CA (1957 TO DATE)  
3 REFERENCES IN FILE CAPLUS (1957 TO DATE)

REFERENCE 1: 135:318588

REFERENCE 2: 134:115733

REFERENCE 3: 132:108101

=> fil uspatall

FILE 'USPATFULL' ENTERED AT 08:52:53 ON 12 MAY 2003  
CA INDEXING COPYRIGHT (C) 2003 AMERICAN CHEMICAL SOCIETY (ACS)

FILE 'USPAT2' ENTERED AT 08:52:53 ON 12 MAY 2003  
CA INDEXING COPYRIGHT (C) 2003 AMERICAN CHEMICAL SOCIETY (ACS)

=> d bib abs hitstr tot 118

L18 ANSWER 1 OF 3 USPATFULL  
 AN 2002:280844 USPATFULL  
 TI Ligands for metals and improved metal-catalyzed processes based thereon  
 IN Buchwald, Stephen L., Newton, MA, UNITED STATES  
     Old, David W., Somerville, MA, UNITED STATES  
     Wolfe, John P., Brighton, MA, UNITED STATES  
     Palucki, Michael, Belle Meade, NJ, UNITED STATES  
     Kamikawa, Ken, Brookline, MA, UNITED STATES  
 PI US 2002156295 A1 20021024  
 AI US 2001-4101 A1 20011023 (10)  
 RLI Continuation of Ser. No. US 1999-231315, filed on 13 Jan 1999, GRANTED,  
     Pat. No. US 6307087 Continuation-in-part of Ser. No. US 1998-113478,  
     filed on 10 Jul 1998, GRANTED, Pat. No. US 6395916  
 DT Utility  
 FS APPLICATION  
 LREP FOLEY HOAG LLP, PATENT GROUP, 155 SEAPORT BOULEVARD, BOSTON, MA, 02110  
 CLMN Number of Claims: 86  
 ECL Exemplary Claim: 1  
 DRWN 1 Drawing Page(s)  
 LN.CNT 4415  
 CAS INDEXING IS AVAILABLE FOR THIS PATENT.  
 AB One aspect of the present invention relates to novel ligands for  
     transition metals. A second aspect of the present invention relates to  
     the use of catalysts comprising these ligands in transition  
     metal-catalyzed carbon-heteroatom and carbon-carbon bond-forming  
     reactions. The subject methods provide improvements in many features of  
     the transition metal-catalyzed reactions, including the range of

suitable substrates, reaction conditions, and efficiency.

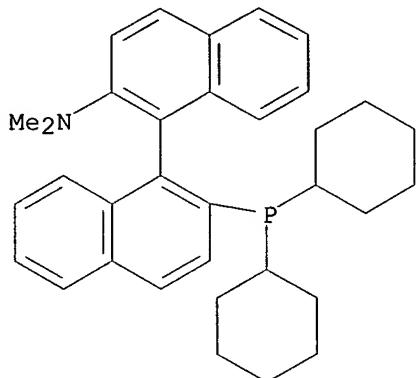
CAS INDEXING IS AVAILABLE FOR THIS PATENT.

IT 255882-15-6 255882-16-7

(catalyst; prepn. of biaryl phosphine and amine ligands for improved palladium-catalyzed amination reactions, Suzuki couplings, arylations, vinylations, and carbon-oxygen bond formation reactions)

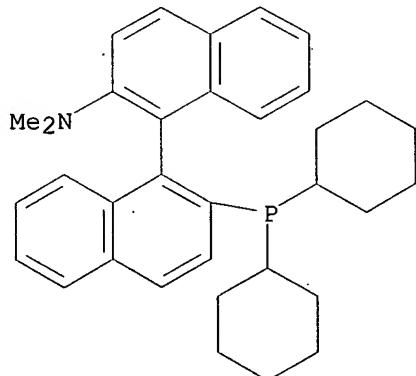
RN 255882-15-6 USPATFULL

CN [1,1'-Binaphthalen]-2-amine, 2'-(dicyclohexylphosphino)-N,N-dimethyl-,  
(R) - (9CI) (CA INDEX NAME)



RN 255882-16-7 USPATFULL

CN [1,1'-Binaphthalen]-2-amine, 2'-(dicyclohexylphosphino)-N,N-dimethyl-,  
(S) - (9CI) (CA INDEX NAME)

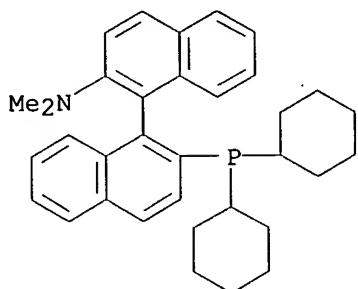


IT 255835-81-5P

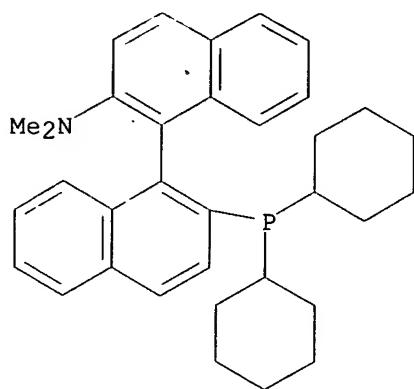
(prepd. catalyst; prepn. of biaryl phosphine and amine ligands for improved palladium-catalyzed amination reactions, Suzuki couplings, arylations, vinylations, and carbon-oxygen bond formation reactions)

RN 255835-81-5 USPATFULL

CN [1,1'-Binaphthalen]-2-amine, 2'-(dicyclohexylphosphino)-N,N-dimethyl-  
(9CI) (CA INDEX NAME)

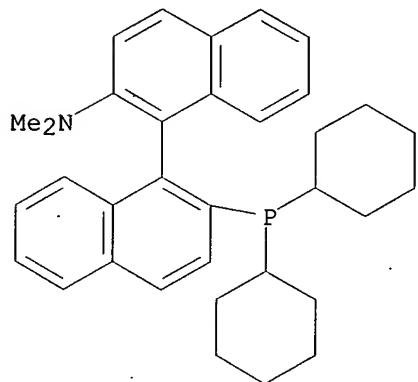


L18 ANSWER 2 OF 3 USPATFULL  
 AN 2002:122783 USPATFULL  
 TI Ligands for metals and improved metal-catalyzed processes based thereon  
 IN Buchwald, Stephen L., Newton, MA, United States  
 Wolfe, John P., Brighton, MA, United States  
 Old, David W., Somerville, MA, United States  
 Kamikawa, Ken, Brookline, MA, United States  
 Palucki, Michael, Belle Meade, NJ, United States  
 PA Massachusetts Institute of Technology, Cambridge, MA, United States  
 (U.S. corporation)  
 PI US 6395916 B1 20020528  
 AI US 1998-113478 19980710 (9)  
 DT Utility  
 FS GRANTED  
 EXNAM Primary Examiner: Higel, Floyd D.; Assistant Examiner: Sackey, Ebenezer  
 LREP Gordon, Dana M., Foley, Hoag & Eliot LLP  
 CLMN Number of Claims: 43  
 ECL Exemplary Claim: 1  
 DRWN 0 Drawing Figure(s); 0 Drawing Page(s)  
 LN.CNT 4455  
 CAS INDEXING IS AVAILABLE FOR THIS PATENT.  
 AB One aspect of the present invention relates to novel, electron-rich bidentate ligands for transition metals. A second aspect of the present invention relates to the use of catalysts comprising these ligands in transition metal-catalyzed carbon-heteroatom and carbon-carbon bond-forming reactions. The subject methods provide improvements in many features of the transition metal-catalyzed reactions, including the range of suitable substrates, reaction conditions, and efficiency.  
 CAS INDEXING IS AVAILABLE FOR THIS PATENT.  
 IT 255882-15-6 255882-16-7  
 (catalyst; prepn. of biaryl phosphine and amine ligands for improved palladium-catalyzed amination reactions, Suzuki couplings, arylations, vinylations, and carbon-oxygen bond formation reactions)  
 RN 255882-15-6 USPATFULL  
 CN [1,1'-Binaphthalen]-2-amine, 2'-(dicyclohexylphosphino)-N,N-dimethyl-, (R)- (9CI) (CA INDEX NAME)



RN 255882-16-7 USPATFULL

CN [1,1'-Binaphthalen]-2-amine, 2'-(dicyclohexylphosphino)-N,N-dimethyl-,  
(S)- (9CI) (CA INDEX NAME)

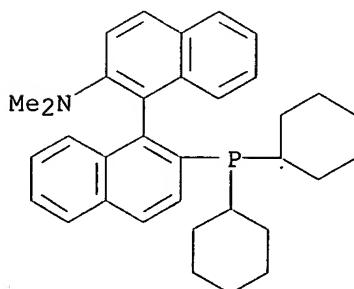


IT 255835-81-5P

(prepd. catalyst; prepn. of biaryl phosphine and amine ligands for improved palladium-catalyzed amination reactions, Suzuki couplings, arylations, vinylations, and carbon-oxygen bond formation reactions)

RN 255835-81-5 USPATFULL

CN [1,1'-Binaphthalen]-2-amine, 2'-(dicyclohexylphosphino)-N,N-dimethyl-  
(9CI) (CA INDEX NAME)

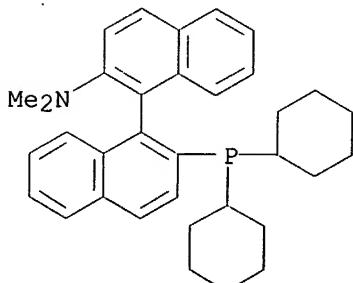


L18 ANSWER 3 OF 3 USPATFULL  
AN 2001:185515 USPATFULL

TI Ligands for metals and improved metal-catalyzed processes based thereon  
 IN Buchwald, Stephen L., Newton, MA, United States  
 Old, David W., Somerville, MA, United States  
 Wolfe, John P., Brighton, MA, United States  
 Palucki, Michael, Belle Meade, NJ, United States  
 Kamikawa, Ken, Brookline, MA, United States  
 PA Massachusetts Institute of Technology, Cambridge, MA, United States  
 (U.S. corporation)  
 PI US 6307087 B1 20011023  
 AI US 1999-231315 19990113 (9)  
 RLI Continuation-in-part of Ser. No. US 1998-113478, filed on 10 Jul 1998  
 DT Utility  
 FS GRANTED  
 EXNAM Primary Examiner: Higel, Floyd D.; Assistant Examiner: Sackey, Ebenezer  
 LREP Gordon, Dana M. Foley Hoag & Eliot LLP  
 CLMN Number of Claims: 84  
 ECL Exemplary Claim: 1  
 DRWN 1 Drawing Figure(s); 1 Drawing Page(s)  
 LN.CNT 4650  
 CAS INDEXING IS AVAILABLE FOR THIS PATENT.  
 AB One aspect of the present invention relates to novel ligands for transition metals. A second aspect of the present invention relates to the use of catalysts comprising these ligands in transition metal-catalyzed carbon-heteroatom and carbon-carbon bond-forming reactions. The subject methods provide improvements in many features of the transition metal-catalyzed reactions, including the range of suitable substrates, reaction conditions, and efficiency.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

IT 255835-81-5P  
 (biaryl phosphine and amine ligands for improved transition metal-catalyzed processes)  
 RN 255835-81-5 USPATFULL  
 CN [1,1'-Binaphthalen]-2-amine, 2'-(dicyclohexylphosphino)-N,N-dimethyl-  
 (9CI) (CA INDEX NAME)



=> fil hcaplus  
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FILE COVERS 1907 - 12 May 2003 VOL 138 ISS 20  
FILE LAST UPDATED: 11 May 2003 (20030511/ED)

This file contains CAS Registry Numbers for easy and accurate substance identification.

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L17 ANSWER 1 OF 7 HCAPLUS COPYRIGHT 2003 ACS  
AN 2002:879182 HCAPLUS  
DN 138:221639  
TI Synthesis of aminophosphine ligands with binaphthyl backbones for silver(I)-catalyzed enantioselective allylation of benzaldehyde  
AU Wang, Yi; Ji, Bao-Ming; Ding, Kui-Ling  
CS State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai, 200032, Peop. Rep. China  
SO Chinese Journal of Chemistry (2002), 20(11), 1300-1312  
CODEN: CJOCEV; ISSN: 1001-604X  
PB Science Press  
DT Journal  
LA English  
CC 29-7 (Organometallic and Organometalloidal Compounds)  
Section cross-reference(s): 67  
OS CASREACT 138:221639  
AB Aminophosphine ligands with binaphthalene and octahydrobinaphthalene backbones were synthesized from 2-amino-2'-hydroxy-1,1'-binaphthyl (NOBIN) and 2-amino-2'-hydroxy-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl (H8-NOBIN), resp. Asym. induction efficiency of silver(I)-ligand complexes was exampd. for allylation of benzaldehyde with allyltributyltin, yielding 4-phenyl-4-hydroxy-1-butene (1). For example, (S)-1 was obtained (100% yield, 54.5% ee) under optimized reaction conditions via allylation catalyzed by silver(I)/(S)-(+)2-pyrrolidino-2'-diphenylphosphino-1,1'-binaphthyl complex. Effects of binaphthyl backbone chirality and substituents at chelating N, P atoms on enantioselectivity are discussed.  
ST aminophosphine binaphthyl octahydrobinaphthyl prepn allylation catalyst; benzaldehyde stereoselective allylation allyltin silver aminophosphinyl binaphthalene catalyzed  
IT Allylation catalysts  
Asymmetric synthesis and induction  
(prep. of aminophosphine ligands with binaphthalene and octahydronaphthalene backbones for silver-catalyzed enantioselective allylation of benzaldehyde with allyltributyltin)  
IT Phosphines  
RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation); USES (Uses)  
(prep. of aminophosphine ligands with binaphthalene and octahydronaphthalene backbones for silver-catalyzed enantioselective allylation of benzaldehyde with allyltributyltin)  
IT Allylation  
(stereoselective; prep. of aminophosphine ligands with binaphthalene and octahydronaphthalene backbones for silver-catalyzed enantioselective allylation of benzaldehyde with allyltributyltin)  
IT 2923-28-6 14104-20-2 26042-63-7 216368-93-3 328074-69-7  
328074-70-0 328074-72-2 328074-73-3 328074-79-9  
RL: CAT (Catalyst use); USES (Uses)

(prep. of aminophosphine ligands with binaphthalene and octahydronaphthalene backbones for silver-catalyzed enantioselective allylation of benzaldehyde with allyltributyltin)

IT 255882-15-6P 413578-90-2P 413578-93-5P 413578-94-6P  
 413578-97-9P 413578-98-0P 500718-20-7P 500718-21-8P 500718-22-9P  
 500718-23-0P  
 RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation);  
 USES (Uses)  
 (prep. of aminophosphine ligands with binaphthalene and octahydronaphthalene backbones for silver-catalyzed enantioselective allylation of benzaldehyde with allyltributyltin)

IT 100-52-7, Benzaldehyde, reactions 110-52-1 2409-61-2 4559-70-0  
 6737-42-4 14717-29-4 24850-33-7 55933-41-0 145290-34-2  
 187344-92-9 216368-90-0 278800-79-6 311800-97-2 325797-63-5  
 326921-37-3 413578-87-7  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (prep. of aminophosphine ligands with binaphthalene and octahydronaphthalene backbones for silver-catalyzed enantioselective allylation of benzaldehyde with allyltributyltin)

IT 166276-11-5P 216368-92-2P 413578-86-6P 413578-89-9P 413578-91-3P  
 413578-92-4P 413578-95-7P 413578-96-8P 500718-24-1P 500718-25-2P  
 500718-26-3P 500718-27-4P 500718-28-5P 500718-30-9P 500718-31-0P  
 500718-32-1P  
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)  
 (prep. of aminophosphine ligands with binaphthalene and octahydronaphthalene backbones for silver-catalyzed enantioselective allylation of benzaldehyde with allyltributyltin)

IT 77118-87-7P 85551-57-1P  
 RL: SPN (Synthetic preparation); PREP (Preparation)  
 (prep. of aminophosphine ligands with binaphthalene and octahydronaphthalene backbones for silver-catalyzed enantioselective allylation of benzaldehyde with allyltributyltin)

RE.CNT 34 THERE ARE 34 CITED REFERENCES AVAILABLE FOR THIS RECORD

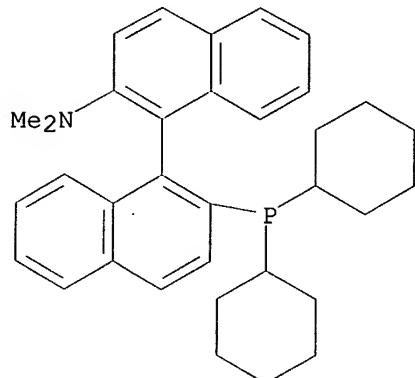
RE

- (1) Aoki, S; Tetrahedron 1993, V49, P1783 HCPLUS
- (2) Boldrini, G; J Chem Soc, Chem Commun 1986, P685 HCPLUS
- (3) Brown, H; J Am Chem Soc 1983, V105, P2092 HCPLUS
- (4) Corey, E; J Am Chem Soc 1989, V111, P5495 HCPLUS
- (5) Costa, A; J Am Chem Soc 1993, V115, P7001 HCPLUS
- (6) Ding, K; Chem Commun 1997, P693 HCPLUS
- (7) Ding, K; Chem Eur J 1999, V5, P1734 HCPLUS
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- (18) Marshall, J; Synlett 1992, P653 HCPLUS
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- (24) Roush, W; J Am Chem Soc 1988, V110, P3979 HCPLUS
- (25) Schmidt, B; Angew Chem, Int Ed Engl 1991, V30, P99
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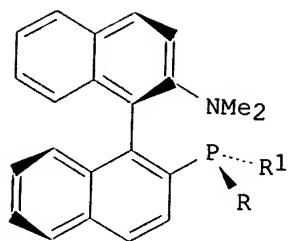
(29) Wang, Y; Tetrahedron Lett 2002, V43, P159 HCPLUS  
 (30) Wang, Y; Tetrahedron: Asymmetry 2000, V11, P4153 HCPLUS  
 (31) Yanagisawa, A; Comprehensive Asymmetric Catalysis 1999, VII  
 (32) Yanagisawa, A; J Am Chem Soc 1996, V118, P4723 HCPLUS  
 (33) Yanagisawa, A; Synlett 1997, P88 HCPLUS  
 (34) Yanagisawa, A; Synlett 1997, P933 HCPLUS

IT 255882-15-6P  
 RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation);  
 USES (Uses)  
 (prepn. of aminophosphine ligands with binaphthalene and  
 octahydronaphthalene backbones for silver-catalyzed enantioselective  
 allylation of benzaldehyde with allyltributyltin)

RN 255882-15-6 HCPLUS  
 CN [1,1'-Binaphthalen]-2-amine, 2'-(dicyclohexylphosphino)-N,N-dimethyl-,  
 (R)- (9CI) (CA INDEX NAME)



L17 ANSWER 2 OF 7 HCPLUS COPYRIGHT 2003 ACS  
 AN 2002:116711 HCPLUS  
 DN 136:309970  
 TI P-Chirogenic Binaphthyl-Substituted Monophosphines: Synthesis and Use in  
 Enolate Vinylation/Arylation Reactions  
 AU Hamada, Takayuki; Buchwald, Stephen L.  
 CS Department of Chemistry, Massachusetts Institute of Technology, Cambridge,  
 MA, 02139, USA  
 SO Organic Letters (2002), 4(6), 999-1001  
 CODEN: ORLEF7; ISSN: 1523-7060  
 PB American Chemical Society  
 DT Journal  
 LA English  
 CC 29-7 (Organometallic and Organometalloidal Compounds)  
 Section cross-reference(s): 24, 75  
 OS CASREACT 136:309970  
 GI



AB New phosphine ligands I ( $R = Ph$ ,  $R1 = t\text{-Bu}$ ;  $R = t\text{-Bu}$ ,  $R1 = Ph$ ) possessing both axial chirality and a chirogenic phosphorus center were prep'd. from ( $R$ )-2-bromo-2'-N,N-(dimethylamino)-1,1'-binaphthyl via a simple Li-halogen exchange protocol. The asym. vinylation of a ketone enolate with ( $R$ , $RP$ )-2-(tert-butylphenylphosphino)-2'-N,N-(dimethylamino)-1,1'-binaphthyl I ( $R = Ph$ ,  $R1 = t\text{-Bu}$ ) afforded the coupling product with good enantiomeric excess.

ST chirogenic binaphthyl phosphine prep'n cocatalyst enolate vinylation arylation; crystal mol structure tert butylphenylphosphino dimethylamino binaphthyl; asym vinylation arylation ketone enolate palladium amino phosphino binaphthyl

IT Crystal structure  
Molecular structure  
(of tert-butylphenylphosphino(dimethylamino)binaphthyl)

IT Arylation catalysts  
Asymmetric synthesis and induction  
Vinylation catalysts  
(prep'n. of phosphorus-chirogenic binaphthyl-substituted monophosphines and their use in enolate vinylation/arylation reactions)

IT 410083-22-6P  
RL: CAT (Catalyst use); PRP (Properties); RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent); USES (Uses)  
(crystal structure; prep'n. of phosphorus-chirogenic binaphthyl-substituted monophosphines and their use in enolate vinylation/arylation reactions)

IT 410071-71-5P 410084-17-2P  
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)  
(prep'n. and phosphine deprotection of)

IT 410083-24-8P 410083-25-9P  
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)  
(prep'n. and redn. of)

IT 350249-40-0P 405876-99-5P  
RL: SPN (Synthetic preparation); PREP (Preparation)  
(prep'n. of)

IT 255882-15-6  
RL: CAT (Catalyst use); USES (Uses)  
(prep'n. of phosphorus-chirogenic binaphthyl-substituted monophosphines and their use in enolate vinylation/arylation reactions)

IT 410083-23-7P  
RL: CAT (Catalyst use); RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent); USES (Uses)  
(prep'n. of phosphorus-chirogenic binaphthyl-substituted monophosphines and their use in enolate vinylation/arylation reactions)

IT 590-15-8 591-17-3 6057-79-0, tert-Butyl(phenyl)phosphine oxide  
29949-69-7, tert-Butyl(chloro)phenylphosphine 350251-14-8 405877-16-9  
RL: RCT (Reactant); RACT (Reactant or reagent)

(prepn. of phosphorus-chirogenic binaphthyl-substituted monophosphines  
and their use in enolate vinylation/arylation reactions)

RE.CNT 29 THERE ARE 29 CITED REFERENCES AVAILABLE FOR THIS RECORD  
RE

- (1) Burk, M; J Am Chem Soc 1993, V115, P10125 HCPLUS
- (2) Chieffi, A; Org Lett 2001, V3, P1897 HCPLUS
- (3) Coumbe, T; Tetrahedron Lett 1994, V35, P625 HCPLUS
- (4) Hamada, T; J Am Chem Soc 2002, V124, P1261 HCPLUS
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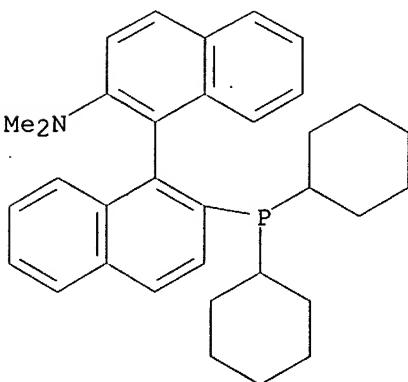
IT 255882-15-6

RL: CAT (Catalyst use); USES (Uses)

(prepn. of phosphorus-chirogenic binaphthyl-substituted monophosphines  
and their use in enolate vinylation/arylation reactions)

RN 255882-15-6 HCPLUS

CN [1,1'-Binaphthalen]-2-amine, 2'-(dicyclohexylphosphino)-N,N-dimethyl-,  
(R)- (9CI) (CA INDEX NAME)

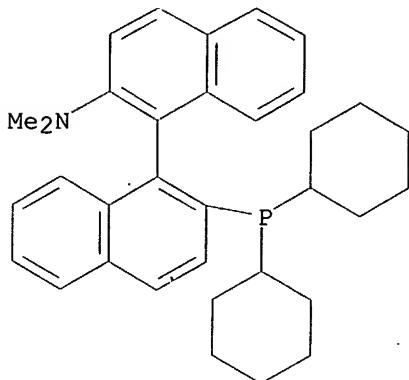


AU Hamada, Takayuki; Chieffi, Andre; Ahman, Jens; Buchwald, Stephen L.  
 CS Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA, 02139, USA  
 SO Journal of the American Chemical Society (2002), 124(7), 1261-1268  
 CODEN: JACSAT; ISSN: 0002-7863  
 PB American Chemical Society  
 DT Journal  
 LA English  
 CC 24-4 (Alicyclic Compounds)  
 AB A new catalyst system for the enantioselective .alpha.-arylation of ketones is reported. This catalyst, prepd. from Pd2(dba)3 and a bulky dialkylphosphino-binaphthyl ligand, is able to effect the asym. arylation of ketone enolates with aryl bromides utilizing NaOtBu as base. These new catalysts enjoy much higher reactivity than previous systems; arylation reactions could be effected at room temp. with only 2 mol % of the Pd catalyst. The coupling of .alpha.-alkyl-.alpha.'-protected cyclopentanones proceeded in high yield, and the resulting quaternary stereogenic center was installed in up to 94% ee.  
 ST asym arylation enolate palladium dialkylphosphinobinaphthyl; cyclopentanone enolate asym arylation palladium dialkylphosphinobinaphthyl  
 IT Enolates  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
     (improved catalyst for asym. arylation of ketone enolates)  
 IT Arylation  
 Arylation catalysts  
     (stereoselective; improved catalyst for asym. arylation of ketone enolates)  
 IT 3375-31-3, Palladium diacetate 51364-51-3 55700-44-2 76189-56-5,  
     (S)-BINAP 134484-36-9 139139-92-7 149341-34-4, (R)-QUINAP  
 255882-16-7 255882-18-9 350251-12-6 405877-62-5  
 RL: CAT (Catalyst use); USES (Uses)  
     (improved catalyst for asym. arylation of ketone enolates)  
 IT 405877-65-8P 405877-66-9P 405877-67-0P 405877-68-1P 405877-69-2P  
 405877-70-5P 405877-71-6P  
 RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation);  
     USES (Uses)  
     (improved catalyst for asym. arylation of ketone enolates)  
 IT 95-46-5, o-Tolyl bromide 104-92-7, p-Bromoanisole 106-38-7, p-Tolyl  
     bromide 402-43-7 591-17-3, m-Tolyl bromide 1120-72-5,  
     2-Methylcyclopentanone 2398-37-0, m-Bromoanisole 3972-65-4  
     17789-14-9 53753-58-5, Diisopropylphosphine oxide 128544-05-8  
     405877-72-7  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
     (improved catalyst for asym. arylation of ketone enolates)  
 IT 405877-15-8P 405877-16-9P 405877-17-0P 405877-18-1P 405877-63-6P  
 405877-64-7P  
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT  
     (Reactant or reagent)  
     (improved catalyst for asym. arylation of ketone enolates)  
 IT 22800-17-5P 405876-97-3P 405876-98-4P 405876-99-5P 405877-00-1P  
 405877-01-2P 405877-02-3P 405877-03-4P 405877-04-5P 405877-05-6P  
 405877-06-7P 405877-07-8P 405877-08-9P 405877-09-0P 405877-10-3P  
 405877-11-4P 405877-12-5P 405877-13-6P 405877-14-7P  
 RL: SPN (Synthetic preparation); PREP (Preparation)  
     (improved catalyst for asym. arylation of ketone enolates)  
 IT 100-61-8, N-Methylaniline, reactions  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
     (reaction with 2-formyl-5-methylcyclopentanone)  
 IT 109-94-4, Ethyl formate  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
     (reaction with 2-methylcyclopentanone)  
 RE.CNT 63 THERE ARE 63 CITED REFERENCES AVAILABLE FOR THIS RECORD

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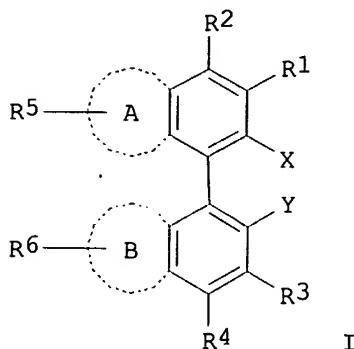
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 (63) Yin, J; Submitted for publication  
 IT 255882-16-7  
 RL: CAT (Catalyst use); USES (Uses)  
 (improved catalyst for asym. arylation of ketone enolates)  
 RN 255882-16-7 HCAPLUS  
 CN [1,1'-Binaphthalen]-2-amine, 2'-(dicyclohexylphosphino)-N,N-dimethyl-,  
 (S)- (9CI) (CA INDEX NAME)



L17 ANSWER 4 OF 7 HCAPLUS COPYRIGHT 2003 ACS  
 AN 2001:772171 HCAPLUS  
 DN 135:318588  
 TI Biaryl phosphine and amine ligands for improved transition metal-catalyzed processes  
 IN Buchwald, Stephen L.; Old, David W.; Wolfe, John P.; Palucki, Michael; Kamikawa, Ken  
 PA Massachusetts Institute of Technology, USA  
 SO U.S., 55 pp., Cont.-in-part of U.S. Ser. No. 113,478.  
 CODEN: USXXAM  
 DT Patent  
 LA English  
 IC ICM C07C255-03  
 ICS C07F009-28; C07D265-30; C07D211-70; C07D209-04  
 NCL 558388000  
 CC 29-7 (Organometallic and Organometalloidal Compounds)  
 Section cross-reference(s): 25  
 FAN.CNT 2

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	US 6307087	B1	20011023	US 1999-231315	19990113 <--
	US 6395916	B1	20020528	US 1998-113478	19980710 <--
	CA 2336691	AA	20000120	CA 1999-2336691	19990709 <--
	WO 2000002887	A2	20000120	WO 1999-US15450	19990709 <--
	WO 2000002887	A3	20000629		
	W: CA, JP				
	RW: AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE				
	EP 1097158	A2	20010509	EP 1999-933785	19990709 <--
	R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, FI				
	JP 2002520328	T2	20020709	JP 2000-559117	19990709 <--
	US 2002156295	A1	20021024	US 2001-4101	20011023 <--
PRAI	US 1998-113478	A2	19980710		
	US 1998-196855	A	19981120		
	US 1999-231315	A	19990113		

OS US 1999-239024 A 19990127  
 GI WO 1999-US15450 W 19990709 <--  
 CASREACT 135:318588; MARPAT 135:318588



AB The present invention relates to the prepn. of novel biaryl phosphine and amine ligands (I) [wherein A and B = independently fused monocyclic or polycyclic cycloalkyl, cycloalkenyl, aryl, or heterocyclic rings of 4-8 atoms; X = NR<sub>2</sub>, PR<sub>2</sub>, AsR<sub>2</sub>, OR, or SR; Y = NR<sub>2</sub>, PR<sub>2</sub>, AsR<sub>2</sub>, OR, SR, SiR<sub>3</sub>, alkyl, or H; R-R<sub>6</sub> = independently H, halogen, (hetero)alkyl, alkenyl, alkynyl, hydroxy, alkoxy, silyloxy, amino, nitro, sulfonyl, amide, carbonyl, ketone, anhydride, silyl, thioalkyl, ketone, ester, nitrile, (hetero)aryl, etc.] for transition metals and their use in metal-catalyzed carbon-heteroatom and carbon-carbon bond-forming reactions. Unexpected improvements over the prior art were demonstrated in transition metal-catalyzed aryl amination reactions, Suzuki couplings giving both biaryl and alkylaryl products, arylations and vinylations at the position .alpha. to carbonyl groups, and carbon-oxygen bond formation. The ligands and methods of the invention enable transformations utilizing aryl chlorides and bromides at room temp. at synthetically useful rates with extremely small amts. of catalyst relative to the limiting reagent. For example, coupling of p-chlorobenzonitrile and morpholine was catalyzed by 2.5 mol% Pd<sub>2</sub>(dba)<sub>3</sub>, 7.5 mol% of 2-(N,N-dimethylamino)-2'-(dicyclohexylphosphino)biphenyl, and NaOBu-t in DME at room temp. to provide 4-(4-morpholinyl)benzonitrile in 96% yield. Thus, the subject processes provide improvements in many features of the transition metal-catalyzed reactions, including the range of suitable substrates, reaction conditions, and efficiency.

ST biaryl phosphine amine ligand prepn transition metal catalyst; amination aryl chloride bromide palladium catalysts; Suzuki coupling aryl chloride bromide palladium catalysts; ketone arylation palladium catalysts

IT Amines, preparation  
 RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation); USES (Uses)  
 (arom.; biaryl phosphine and amine ligands for improved transition metal-catalyzed processes)

IT Ketones, preparation  
 RL: SPN (Synthetic preparation); PREP (Preparation)  
 (arom.; biaryl phosphine and amine ligands for improved transition metal-catalyzed processes)

IT Aryl halides  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (aryl chlorides; biaryl phosphine and amine ligands for improved transition metal-catalyzed processes)

IT Chlorides, reactions  
 RL: RCT (Reactant); RACT (Reactant or reagent)

(aryl; biaryl phosphine and amine ligands for improved transition metal-catalyzed processes)

IT Amination  
 Amination catalysts  
 Arylation  
 Arylation catalysts  
 Cross-coupling reaction catalysts  
 Suzuki coupling reaction  
 (biaryl phosphine and amine ligands for improved transition metal-catalyzed processes)

IT Phosphines  
 RL: CAT (Catalyst use); USES (Uses)  
 (biaryl phosphine and amine ligands for improved transition metal-catalyzed processes)

IT Biaryls  
 RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation); USES (Uses)  
 (biaryl phosphine and amine ligands for improved transition metal-catalyzed processes)

IT Aryl bromides  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (biaryl phosphine and amine ligands for improved transition metal-catalyzed processes)

IT Transition metal complexes  
 RL: CAT (Catalyst use); USES (Uses)  
 (phosphine; biaryl phosphine and amine ligands for improved transition metal-catalyzed processes)

IT Phosphines  
 RL: CAT (Catalyst use); USES (Uses)  
 (transition metal complexes; biaryl phosphine and amine ligands for improved transition metal-catalyzed processes)

IT 127-09-3, Sodium acetate 534-17-8 584-08-7, Potassium carbonate 3375-31-3, Palladium diacetate 6476-37-5, Dicyclohexylphenylphosphine 7778-53-2 7789-23-3, Potassium fluoride 13400-13-0, Cesium fluoride 14221-01-3, Tetrakis(triphenylphosphine)palladium 51364-51-3, Tris(dibenzylideneacetone)dipalladium 54000-83-8, 2,6-Dimethoxyphenyl-di-t-butylphosphine 166330-10-5 213774-71-1 255837-14-0, 2,4,6-Trimethoxyphenyl-di-t-butylphosphine  
 RL: CAT (Catalyst use); USES (Uses)  
 (biaryl phosphine and amine ligands for improved transition metal-catalyzed processes)

IT 213697-53-1P 224311-51-7P, 2-(Di-tert-butylphosphino)biphenyl 255835-81-5P 255835-82-6P  
 RL: CAT (Catalyst use); IMF (Industrial manufacture); SPN (Synthetic preparation); PREP (Preparation); USES (Uses)  
 (biaryl phosphine and amine ligands for improved transition metal-catalyzed processes)

IT 4688-76-0P 20837-12-1P 59734-92-8P 75295-57-7P 89291-23-6P 128796-39-4P, 4-(Trifluoromethyl)phenylboronic acid 157282-19-4P 213697-67-7P 224311-57-3P 224311-58-4P 224311-59-5P 255837-15-1P, 2-Bromo-4'(trifluoromethyl)biphenyl 255837-16-2P  
 RL: IMF (Industrial manufacture); RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)  
 (biaryl phosphine and amine ligands for improved transition metal-catalyzed processes)

IT 92-69-3P, 4-Hydroxybiphenyl 92-91-1P, 4-Acetyl biphenyl 92-93-3P, 4-Nitrobiphenyl 612-75-9P, 3,3'-Dimethylbiphenyl 613-37-6P 644-08-6P 720-75-2P 825-55-8P, 2-Phenylthiophene 2142-66-7P, 2-Acetyl biphenyl 2920-38-9P, 4-Cyanobiphenyl 2928-43-0P, 2-Hydroxymethylbiphenyl 3976-34-9P, 2,6-Dimethylbiphenyl 4075-79-0P, n-Acetyl-4-aminobiphenyl 5405-15-2P 7372-85-2P, 2,5-Dimethylbiphenyl 10282-31-2P 17057-88-4P 19853-10-2P, [1,1'-Biphenyl]-2-acetonitrile 23676-05-3P 31144-33-9P 39253-43-5P 39910-98-0P, n-(4-Acetylphenyl)morpholine 54660-04-7P,

n-(4-Methoxyphenyl)pyrrolidine 76650-29-8P 76708-78-6P 81693-80-3P  
 82749-62-0P 92495-53-9P 138900-16-0P, N-(4-Fluorophenyl)indole  
 167283-32-1P, N-(4-Methylphenyl)indole 171092-38-9P,  
 3-(3-Acetylphenyl)pyridine 174307-96-1P 180336-54-3P,  
 N-(2,5-Dimethylphenyl)-N-methylaniline 197172-67-1P 213697-51-9P,  
 n-(2,5-Dimethylphenyl)morpholine 213697-52-0P 213697-65-5P  
 213697-66-6P 224311-54-0P 224311-55-1P 251320-77-1P 251320-78-2P  
 251320-81-7P, 3-Acetyl-3',5'-dimethoxybiphenyl 251320-82-8P,  
 4-Carbomethoxy-3'-acetyl biphenyl 251320-84-0P 255835-83-7P,  
 2(Di-t-butylphosphino)-4'-(trifluoromethyl)biphenyl 255835-84-8P  
 255835-85-9P 255882-14-5P

RL: IMF (Industrial manufacture); SPN (Synthetic preparation); PREP (Preparation)

(biaryl phosphine and amine ligands for improved transition metal-catalyzed processes)

IT 95-72-7 98-80-6 99-90-1 99-91-2 100-00-5, 1-Chloro-4-nitrobenzene  
 100-46-9, Benzylamine, reactions 100-61-8, n-Methylaniline, reactions  
 103-88-8, 4'-Bromoacetanilide 106-38-7 106-41-2, 4-Bromophenol  
 106-43-4 106-49-0, p-Toluidine, reactions 108-94-1, Cyclohexanone,  
 reactions 110-91-8, Morpholine, reactions 111-26-2, Hexylamine  
 111-92-2, Dibutylamine 120-72-9, Indole, reactions 123-75-1,  
 Pyrrolidine, reactions 402-43-7, 4-(Trifluoromethyl)phenyl bromide  
 460-00-4, 1-Bromo-4-fluorobenzene 553-94-6, 2-Bromo-p-xylene 556-96-7  
 563-80-4 565-69-5 576-22-7 583-53-9, 1,2-Dibromobenzene 583-55-1,  
 2-Bromoiodobenzene 592-41-6, 1-Hexene, reactions 619-42-1 623-03-0,  
 4-Chlorobenzonitrile 623-12-1 626-60-8, 3-Chloropyridine 698-00-0  
 768-90-1, 1-Bromoadamantane 1003-09-4, 2-Bromothiophene 1013-88-3,  
 Benzophenone imine 1079-66-9, Chlorodiphenylphosphine 1122-91-4,  
 4-Bromobenzaldehyde 1126-46-1 2052-07-5, 2-Bromobiphenyl 2142-68-9,  
 2'-Chloroacetophenone 2856-63-5, 2-Chlorobenzyl cyanide 3972-65-4,  
 1-Bromo-4-t-butylbenzene 5720-06-9 7051-16-3 13716-10-4,  
 Chlorodi-tert-butylphosphine 16523-54-9, Chlorodicyclohexylphosphine  
 17933-03-8 18982-54-2, 2-Bromobenzylalcohol 22237-13-4,  
 4-Ethoxyphenylboronic acid 40138-16-7 42371-64-2 53847-33-9  
 74866-28-7, 2,2'-Dibromo-1,1'-binaphthyl 204841-19-0, 3-Acetylphenyl  
 boronic acid 251320-89-5, 2-(Bromo)-2'-(isopropyl)biphenyl

RL: RCT (Reactant); RACT (Reactant or reagent)

(biaryl phosphine and amine ligands for improved transition metal-catalyzed processes)

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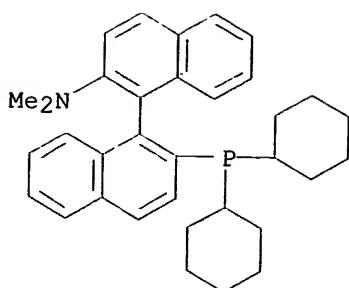
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IT 255835-81-5P

RL: CAT (Catalyst use); IMF (Industrial manufacture); SPN (Synthetic preparation); PREP (Preparation); USES (Uses)  
 (biaryl phosphine and amine ligands for improved transition metal-catalyzed processes)

RN 255835-81-5 HCAPLUS

CN [1,1'-Binaphthalen]-2-amine, 2'-(dicyclohexylphosphino)-N,N-dimethyl-  
 (9CI) (CA INDEX NAME)



L17 ANSWER 5 OF 7 HCAPLUS COPYRIGHT 2003 ACS  
 AN 2001:355541 HCAPLUS  
 DN 135:107072  
 TI Catalytic Asymmetric Vinylation of Ketone Enolates  
 AU Chieffi, Andre; Kamikawa, Ken; Ahman, Jens; Fox, Joseph M.;  
 Buchwald, Stephen L.  
 CS Department of Chemistry, Massachusetts Institute of Technology, Cambridge,  
 MA, 02139, USA  
 SO Organic Letters (2001), 3(12), 1897-1900  
 CODEN: ORLEF7; ISSN: 1523-7060  
 PB American Chemical Society  
 DT Journal  
 LA English  
 CC 24-1 (Alicyclic Compounds)  
 OS CASREACT 135:107072  
 AB A protocol for the catalytic asym. vinylation of ketone enolates has been developed. Key to the success of this process was the development of new electron-rich chiral monodentate ligands.  
 ST asym vinylation ketone phosphine catalyst  
 IT Asymmetric synthesis and induction  
 Vinylation  
 (catalytic asym. vinylation of ketone enolates)  
 IT Vinylation catalysts  
 (catalytic asym. vinylation of ketone enolates in presence of chiral phosphines)  
 IT Ketones, preparation  
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)  
 (cycloalkanones; catalytic asym. vinylation of ketone enolates)  
 IT Vinyl compounds, reactions  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (halo; catalytic asym. vinylation of ketone enolates)  
 IT 51364-51-3, Pd2(dba)3 213774-71-1  
 RL: CAT (Catalyst use); USES (Uses)  
 (catalytic asym. vinylation of ketone enolates)  
 IT 233752-13-1P 255882-15-6P 255882-16-7P 255882-17-8P  
 255882-18-9P 350251-12-6P  
 RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation);  
 USES (Uses)  
 (catalytic asym. vinylation of ketone enolates)  
 IT 350249-54-6P  
 RL: PUR (Purification or recovery); RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)  
 (catalytic asym. vinylation of ketone enolates)  
 IT 100-61-8, N-Methylaniline, reactions 103-63-9, 2-Bromoethylbenzene  
 513-37-1 583-60-8, 2-Methylcyclohexanone 590-13-6,  
 cis-1-Bromo-1-propene 590-15-8, trans-1-Bromo-1-propene 593-60-2,  
 Bromoethene 1079-66-9, Chlorodiphenylphosphine 1120-72-5,

2-Methylcyclopentanone 1193-70-0, 2-Propylcyclopentanone 1590-08-5,  
 2-Methyl-1-tetralone 3017-69-4 4819-67-4, 2-Pentylcyclopentanone  
 16523-54-9, Chlorodicyclohexylphosphine 17496-14-9, 2-Methyl-1-indanone  
 86688-06-4 224311-59-5 350249-56-8

RL: RCT (Reactant); RACT (Reactant or reagent)

(catalytic asym. vinylation of ketone enolates)

IT 100717-47-3P 255837-20-8P 255837-21-9P 255837-22-0P 350249-40-0P  
 350249-41-1P 350249-42-2P 350249-45-5P 350249-50-2P 350249-53-5P  
 350249-55-7P 350251-13-7P 350251-14-8P

RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT  
 (Reactant or reagent)

(catalytic asym. vinylation of ketone enolates)

IT 197163-99-8P 350249-43-3P 350249-44-4P 350249-46-6P 350249-47-7P  
 350249-48-8P 350249-49-9P 350249-51-3P 350249-52-4P

RL: SPN (Synthetic preparation); PREP (Preparation)

(catalytic asym. vinylation of ketone enolates)

RE.CNT 26 THERE ARE 26 CITED REFERENCES AVAILABLE FOR THIS RECORD

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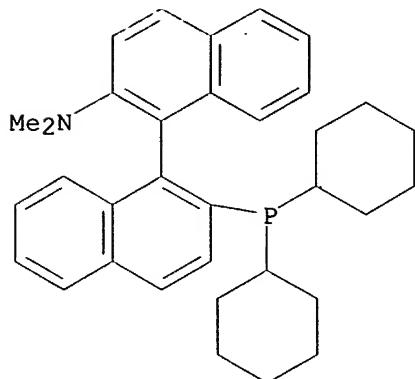
IT 255882-15-6P 255882-16-7P

RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation);  
 USES (Uses)

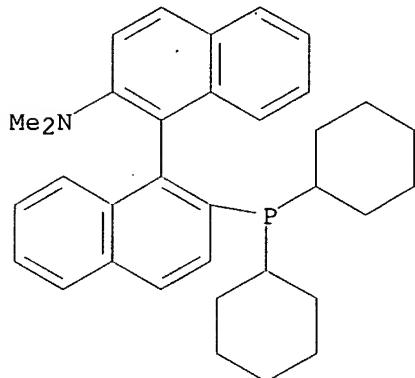
(catalytic asym. vinylation of ketone enolates)

RN 255882-15-6 HCPLUS

CN [1,1'-Binaphthalen]-2-amine, 2'-(dicyclohexylphosphino)-N,N-dimethyl-,  
 (R)- (9CI) (CA INDEX NAME)



RN 255882-16-7 HCPLUS

CN [1,1'-Binaphthalen]-2-amine, 2'-(dicyclohexylphosphino)-N,N-dimethyl-,  
(S)- (9CI) (CA INDEX NAME)

L17 ANSWER 6 OF 7 HCPLUS COPYRIGHT 2003 ACS

AN 2000:792828 HCPLUS

DN 134:115733

TI A Catalytic Asymmetric Suzuki Coupling for the Synthesis of Axially Chiral Biaryl Compounds

AU Yin, Jingjun; Buchwald, Stephen L.

CS Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA, 02139, USA

SO Journal of the American Chemical Society (2000), 122(48), 12051-12052  
CODEN: JACSAT; ISSN: 0002-7863

PB American Chemical Society

DT Journal

LA English

CC 25-22 (Benzene, Its Derivatives, and Condensed Benzenoid Compounds)

OS CASREACT 134:115733

AB Binaphthyl ligands were used for the catalytic asym. Suzuki coupling to form highly enantiomerically enriched biaryl derivs. This is the first example of a catalytic enantioselective cross-coupling reaction that allows the prepn. of functionalized biaryl compds. For example, asym. Suzuki coupling of (1-bromo-2-naphthalenyl)phosphonic acid di-Me ester with (2-methylphenyl)boronic acid in the presence of (+)-(S)-2'-(dicyclohexylphosphino)-N,N-dimethyl-[1,1'-binaphthalen]-2-amine and Pd2(dba)3 gave (+)-[1-(2-methylphenyl)-2-naphthalenyl]phosphonic acid di-Me ester in 95% yield and in 86% enantiomeric excess. Subsequent

phenylation of the latter with phenylmagnesium bromide gave  
 (-)-1-(2-methylphenyl)-2-(diphenylphosphinyl)naphthalene. Redn. of the  
 latter gave (-)-[1-(2-methylphenyl)-2-naphthalenyl]diphenylphosphine.

ST Suzuki coupling phosphinobinaphthalenamine palladium stereochem

IT Coupling reaction catalysts  
 (Suzuki; prepn. of axially chiral biaryl compds. via  
 binaphthyl-catalyzed asym. Suzuki coupling)

IT Stereochemistry  
 Suzuki coupling reaction  
 (prepn. of axially chiral biaryl compds. via binaphthyl-catalyzed asym.  
 Suzuki coupling)

IT Aryl halides  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (prepn. of axially chiral biaryl compds. via binaphthyl-catalyzed asym.  
 Suzuki coupling)

IT 51364-51-3, Pd2(dba)3 98327-87-8 224311-52-8 255835-81-5  
 255882-14-5 255882-16-7, (S)-(+)-2'-(Dicyclohexylphosphino)-N,N-  
 dimethyl[1,1'-binaphthalen]-2-amine 320381-22-4 320381-23-5  
 320767-12-2  
 RL: CAT (Catalyst use); USES (Uses)  
 (prepn. of axially chiral biaryl compds. via Suzuki coupling of  
 arylboronic acids and halobenzene derivs. in presence of palladium and  
 binaphthalene ligand)

IT 88-73-3, 1-Chloro-2-nitrobenzene 577-19-5, 1-Bromo-2-nitrobenzene  
 609-73-4, 1-Iodo-2-nitrobenzene 4688-76-0 16419-60-6,  
 (2-Methylphenyl)boronic acid 89787-12-2, (2-Isopropylphenyl)boronic acid  
 90002-36-1 320381-24-6 320381-25-7  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (prepn. of axially chiral biaryl compds. via Suzuki coupling of  
 arylboronic acids and halobenzene derivs. in presence of palladium and  
 binaphthalene ligand)

IT 100-58-3, Phenylmagnesium bromide 13922-41-3, (1-Naphthalenyl)boronic  
 acid 219834-95-4 320381-26-8  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (prepn. of axially chiral biaryl compds. via binaphthyl-catalyzed asym.  
 Suzuki coupling)

IT 320767-18-8P 320767-21-3P  
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT  
 (Reactant or reagent)  
 (prepn. of axially chiral biaryl compds. via binaphthyl-catalyzed asym.  
 Suzuki coupling)

IT 132532-08-2P 320767-13-3P 320767-14-4P 320767-15-5P 320767-16-6P  
 320767-17-7P 320767-19-9P 320767-20-2P 320767-22-4P  
 RL: SPN (Synthetic preparation); PREP (Preparation)  
 (prepn. of axially chiral biaryl compds. via binaphthyl-catalyzed asym.  
 Suzuki coupling)

RE.CNT 30 THERE ARE 30 CITED REFERENCES AVAILABLE FOR THIS RECORD

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IT 255835-81-5 255882-16-7, (S)-(+)-2'-

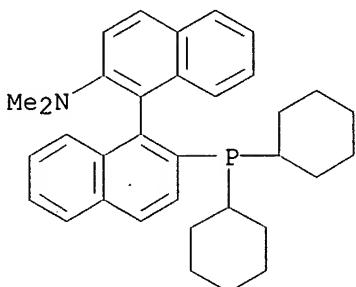
(Dicyclohexylphosphino)-N,N-dimethyl[1,1'-binaphthalen]-2-amine

RL: CAT (Catalyst use); USES (Uses)

(prepn. of axially chiral biaryl compds. via Suzuki coupling of arylboronic acids and halobenzene derivs. in presence of palladium and binaphthalene ligand)

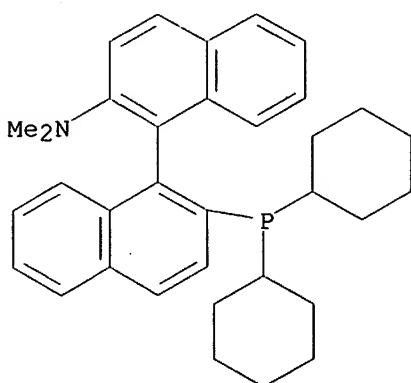
RN 255835-81-5 HCAPLUS

CN [1,1'-Binaphthalen]-2-amine, 2'-(dicyclohexylphosphino)-N,N-dimethyl-, (9CI) (CA INDEX NAME)



RN 255882-16-7 HCAPLUS

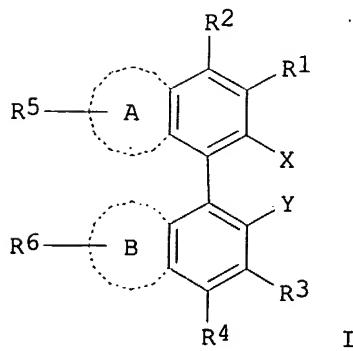
CN [1,1'-Binaphthalen]-2-amine, 2'-(dicyclohexylphosphino)-N,N-dimethyl-, (S)- (9CI) (CA INDEX NAME)



AN 2000:53646 HCAPLUS  
 DN 132:108101  
 TI Biaryl phosphine and amine ligands for improved transition metal-catalyzed processes  
 IN Buchwald, Stephen; Old, David W.; Wolfe, John P.; Palucki, Michael; Kamikawa, Ken; Chieffi, Andrew; Sadighi, Joseph P.; Singer, Robert A.; Ahman, Jens  
 PA Massachusetts Institute of Technology, USA  
 SO PCT Int. Appl., 397 pp.  
 CODEN: PIXXD2  
 DT Patent  
 LA English  
 IC ICM C07F009-02  
 CC 29-7 (Organometallic and Organometalloidal Compounds)  
 Section cross-reference(s): 25

FAN.CNT 2

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	WO 2000002887	A2	20000120	WO 1999-US15450	19990709 <--
	WO 2000002887	A3	20000629		
	W: CA, JP				
	RW: AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE				
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	US 1998-196855	A	19981120		
	US 1999-231315	A	19990113		
	US 1999-239024	A	19990127		
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OS	MARPAT 132:108101				
GI					



AB The present invention relates to the prepn. of novel biaryl phosphine and amine ligands (I) [wherein A and B = independently fused monocyclic or polycyclic cycloalkyl, cycloalkenyl, aryl, or heterocyclic rings of 4-8 atoms; X = NR<sub>2</sub>, PR<sub>2</sub>, AsR<sub>2</sub>, OR, or SR; Y = NR<sub>2</sub>, PR<sub>2</sub>, AsR<sub>2</sub>, OR, SR, SiR<sub>3</sub>, alkyl, or H; R-R<sub>6</sub> = independently H, halogen, (hetero)alkyl, alkenyl, alkynyl, hydroxy, alkoxy, silyloxy, amino, nitro, sulphydryl, amide,

carbonyl, ketone, anhydride, silyl, thioalkyl, ketone, ester, nitrile, (hetero)aryl, etc.) for transition metals and their use in metal-catalyzed carbon-heteroatom and carbon-carbon bond-forming reactions. Unexpected improvements over the prior art were demonstrated in transition metal-catalyzed aryl amination reactions, Suzuki couplings giving both biaryl and alkylaryl products, arylations and vinylations at the position alpha. to carbonyl groups, and carbon-oxygen bond formation. The ligands and methods of the invention enable transformations utilizing aryl chlorides and bromides at room temp. at synthetically useful rates with extremely small amts. of catalyst relative to the limiting reagent. For example, coupling of p-chlorobenzonitrile and morpholine was catalyzed by 2.5 mol% Pd2(dba)3, 7.5 mol% of 2-(N,N-dimethylamino)-2'-  
(dicyclohexylphosphino)biphenyl, and NaOBu-t in DME at room temp. to provide 4-(4-morpholinyl)benzonitrile in 96% yield. Thus, the subject processes provide improvements in many features of the transition metal-catalyzed reactions, including the range of suitable substrates, reaction conditions, and efficiency.

- ST biaryl phosphine ammine ligand prepn transition metal catalyst; amination aryl chloride bromide palladium catalysts; Suzuki coupling aryl chloride bromide palladium catalysts; ketone arylation vinylation palladium catalysts; etherification palladium catalysts.
- IT Amines, preparation
  - RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation); USES (Uses)
    - (arom.; prepn. of biaryl phosphine and amine ligands for improved palladium-catalyzed amination reactions, Suzuki couplings, arylations, vinylations, and carbon-oxygen bond formation reactions)
- IT Ethers, preparation
  - Ketones, preparation
    - RL: SPN (Synthetic preparation); PREP (Preparation)
      - (arom.; prepn. of biaryl phosphine and amine ligands for improved palladium-catalyzed amination reactions, Suzuki couplings, arylations, vinylations, and carbon-oxygen bond formation reactions)
- IT Aryl halides
  - Aryl halides
    - RL: RCT (Reactant); RACT (Reactant or reagent)
      - (aryl chlorides; prepn. of biaryl phosphine and amine ligands for improved palladium-catalyzed amination reactions, Suzuki couplings, arylations, vinylations, and carbon-oxygen bond formation reactions)
- IT Chlorides, reactions
  - Chlorides, reactions
    - RL: RCT (Reactant); RACT (Reactant or reagent)
      - (aryl; prepn. of biaryl phosphine and amine ligands for improved palladium-catalyzed amination reactions, Suzuki couplings, arylations, vinylations, and carbon-oxygen bond formation reactions)
- IT Transition metal complexes
  - Transition metal complexes
    - RL: CAT (Catalyst use); USES (Uses)
      - (phosphine; prepn. of biaryl phosphine and amine ligands for improved palladium-catalyzed amination reactions, Suzuki couplings, arylations, vinylations, and carbon-oxygen bond formation reactions)
- IT Amination
  - Amination catalysts
    - Arylation
      - Arylation catalysts
        - Cross-coupling reaction catalysts
          - Etherification
            - Etherification catalysts
              - Suzuki coupling reaction
                - Vinylation
                  - Vinylation catalysts
                    - (prepn. of biaryl phosphine and amine ligands for improved palladium-catalyzed amination reactions, Suzuki couplings, arylations,

vinylations, and carbon-oxygen bond formation reactions)

IT Phosphines  
 RL: CAT (Catalyst use); USES (Uses)  
 (prepn. of biaryl phosphine and amine ligands for improved palladium-catalyzed amination reactions, Suzuki couplings, arylations, vinylations, and carbon-oxygen bond formation reactions)

IT Biaryls  
 RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation); USES (Uses)  
 (prepn. of biaryl phosphine and amine ligands for improved palladium-catalyzed amination reactions, Suzuki couplings, arylations, vinylations, and carbon-oxygen bond formation reactions)

IT Aryl bromides  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (prepn. of biaryl phosphine and amine ligands for improved palladium-catalyzed amination reactions, Suzuki couplings, arylations, vinylations, and carbon-oxygen bond formation reactions)

IT Phosphines  
 Phosphines  
 RL: CAT (Catalyst use); USES (Uses)  
 (transition metal complexes; prepn. of biaryl phosphine and amine ligands for improved palladium-catalyzed amination reactions, Suzuki couplings, arylations, vinylations, and carbon-oxygen bond formation reactions)

IT 534-17-8, Dicesium carbonate 3375-31-3, Diacetatopalladium 6476-37-5, Dicyclohexylphenylphosphine 14221-01-3, Tetrakis(triphenylphosphine)palladium 31570-04-4 51364-51-3, Tris(dibenzylideneacetone)dipalladium 54000-83-8, 2,6-Dimethoxyphenyl-di-t-butylphosphine 71042-54-1 74286-11-6 76189-56-5 91548-08-2 100165-88-6 133545-16-1 136779-28-7 139139-92-7 145964-33-6 149341-34-4 155806-35-2 213774-71-1 224311-49-3 247940-06-3 255837-14-0, 2,4,6-Trimethoxyphenyl-di-t-butylphosphine 255837-17-3 255837-19-5 255882-15-6 255882-16-7 255882-17-8 255882-18-9  
 RL: CAT (Catalyst use); USES (Uses)  
 (catalyst; prepn. of biaryl phosphine and amine ligands for improved palladium-catalyzed amination reactions, Suzuki couplings, arylations, vinylations, and carbon-oxygen bond formation reactions)

IT 698-00-0P 4688-76-0P 18937-92-3P 20837-12-1P, 2-Bromo-2'-methoxy-1,1'-biphenyl 59734-92-8P 75295-57-7P 89291-23-6P 89787-12-2P, 2-Isopropylphenylboronic acid 128796-39-4P, 4-(Trifluoromethyl)phenylboronic acid 224311-57-3P 224311-58-4P 224311-59-5P 251320-87-3P, 2-Bromo-2'-methylbiphenyl 251320-89-5P, 2-Bromo-2'-isopropylbiphenyl 255837-15-1P, 2-Bromo-4'-(trifluoromethyl)biphenyl 255837-16-2P 255837-18-4P  
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)  
 (intermediate; prepn. of biaryl phosphine and amine ligands for improved palladium-catalyzed amination reactions, Suzuki couplings, arylations, vinylations, and carbon-oxygen bond formation reactions)

IT 213697-53-1P  
 RL: CAT (Catalyst use); RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent); USES (Uses)  
 (prepd. catalyst; prepn. of biaryl phosphine and amine ligands for improved palladium-catalyzed amination reactions, Suzuki couplings, arylations, vinylations, and carbon-oxygen bond formation reactions)

IT 224311-51-7P, 2-(Di-tert-butylphosphino)biphenyl 224311-52-8P 224311-54-0P 224311-55-1P 251320-85-1P, 2-(Dicyclohexylphosphino)-2'-isopropylbiphenyl 251320-86-2P, 2-(Dicyclohexylphosphino)-2'-methylbiphenyl 255835-81-5P 255835-82-6P 255835-83-7P, 2-(Di-t-butylphosphino)-4'-(trifluoromethyl)biphenyl 255835-84-8P, 2-(Di-t-butylphosphino)-2'-(isopropyl)biphenyl 255835-85-9P 255836-32-9P 255836-65-8P 255836-67-0P 255836-68-1P, 1-[2-(Dicyclohexylphosphino)phenyl]naphthalene 255836-69-2P,

1-[2-(Di-t-butylphosphino)phenyl]naphthalene 255882-14-5P  
 RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation);  
 USES (Uses)  
 (prepd. catalyst; prepn. of biaryl phosphine and amine ligands for  
 improved palladium-catalyzed amination reactions, Suzuki couplings,  
 arylations, vinylations, and carbon-oxygen bond formation reactions)

IT 62-53-3, Benzenamine, reactions 75-97-8 88-05-1 88-69-7 90-04-0  
 91-55-4 93-55-0, Propiophenone 95-65-8 95-68-1 95-72-7 96-22-0,  
 3-Pantanone 98-54-4 98-80-6 98-86-2, reactions 99-02-5 99-90-1  
 99-91-2 100-00-5, 1-Chloro-4-nitrobenzene 100-01-6, reactions  
 100-42-5, reactions 100-46-9, Benzenemethanamine, reactions 100-61-8,  
 reactions 103-69-5 103-88-8, 4'-Bromoacetanilide 104-92-7 104-94-9  
 105-53-3, Diethyl malonate 106-38-7 106-39-8 106-41-2, 4-Bromophenol  
 106-43-4 106-49-0, reactions 108-41-8 108-44-1, reactions  
 108-91-8, Cyclohexanamine, reactions 108-94-1, Cyclohexanone, reactions  
 109-01-3 109-04-6 109-09-1 110-89-4, Piperidine, reactions  
 110-91-8, Morpholine, reactions 111-26-2, 1-Hexanamine 111-92-2  
 119-61-9, Benzophenone, reactions 120-72-9, Indole, reactions 122-00-9  
 122-39-4, Diphenylamine, reactions 123-75-1, Pyrrolidine, reactions  
 141-97-9 280-64-8, 9-BBN 392-83-6, 2-Bromobenzotrifluoride 399-52-0  
 402-43-7, 4-(Trifluoromethyl)phenyl bromide 460-00-4,  
 1-Bromo-4-fluorobenzene 502-42-1, Cycloheptanone 504-02-9,  
 1,3-Cyclohexanedione 529-34-0 530-93-8, .beta.-Tetralone 540-88-5,  
 tert-Butyl acetate 553-94-6 556-96-7 557-93-7, 2-Bromopropene  
 563-80-4 565-69-5 565-80-0 576-22-7 576-26-1 583-53-9,  
 1,2-Dibromobenzene 583-55-1, 2-Bromoiodobenzene 586-77-6 588-72-7,  
 trans-.beta.-Bromostyrene 590-15-8, trans-1-Bromopropene 591-20-8  
 592-41-6, 1-Hexene, reactions 615-36-1, 2-Bromoaniline 618-45-1  
 618-89-3 619-42-1 623-00-7, 4-Bromobenzonitrile 623-03-0 623-12-1  
 624-31-7 626-55-1, 3-Bromopyridine 626-60-8, 3-Chloropyridine  
 645-36-3 765-30-0, Cyclopropylamine 766-51-8 766-84-7 778-82-5  
 782-17-2 872-31-1, 3-Bromo thiophene 873-32-5, 2-Chlorobenzonitrile  
 930-29-0, 1-Chlorocyclopentene 931-51-1, Cyclohexylmagnesium chloride  
 948-65-2 1003-09-4, 2-Bromo thiophene 1013-88-3, Benzophenone imine  
 1079-66-9, Chlorodiphenylphosphine 1122-91-4, 4-Bromobenzaldehyde  
 1122-95-8 1126-46-1 1450-65-3 1590-08-5 2038-03-1,  
 4-Morpholineethanamine 2052-07-5, 2-Bromobiphenyl 2142-68-9,  
 2'-Chloroacetophenone 2398-37-0 2635-13-4 2845-89-8 2856-63-5,  
 2-Chlorobenzyl cyanide 2905-65-9 3972-65-4, 1-Bromo-4-t-butylbenzene  
 4079-52-1 4541-32-6 5350-57-2 5619-07-8, DL-Phenylalanine methyl  
 ester hydrochloride 5720-06-9 5798-75-4, Ethyl 4-bromobenzoate  
 5892-99-9 6781-98-2 7051-16-3 7073-94-1, 2-Bromo isopropylbenzene  
 7524-50-7, L-Phenylalanine methyl ester hydrochloride 7598-28-9  
 13716-10-4, Chlorodi-tert-butylphosphine 13922-41-3, 1-Naphthylboronic  
 acid 15499-27-1 16081-16-6 16419-60-6 16523-54-9,  
 Chlorodicyclohexylphosphine 17496-14-9, 2-Methylindanone 17763-70-1  
 17763-80-3 17789-14-9, 2-(3-Bromophenyl)1,3-dioxolane 17933-03-8  
 18982-54-2, 2-Bromobenzyl alcohol 22237-13-4, 4-Ethoxyphenylboronic acid  
 22867-74-9 24544-04-5 27505-78-8 27752-24-5 36800-95-0,  
 4-Cyanophenyl tosylate 40138-16-7, 2-Formylphenylboronic acid  
 41085-43-2, 2-Bromo-3-nitrotoluene 41492-05-1 42371-64-2 53847-33-9  
 66107-29-7 66107-32-2 74866-28-7, 2,2'-Dibromo-1,1'-binaphthyl  
 100379-00-8 100717-47-3 109613-00-5 112042-84-9 154318-75-9  
 157282-19-4 158266-43-4 204841-19-0, 3-Acetylphenylboronic acid  
 207611-58-3 255837-20-8 255837-21-9 255837-22-0 255837-23-1

RL: RCT (Reactant); RACT (Reactant or reagent)  
 (starting material; prepn. of biaryl phosphine and amine ligands for  
 improved palladium-catalyzed amination reactions, Suzuki couplings,  
 arylations, vinylations, and carbon-oxygen bond formation reactions)

IT 78235-91-3P 213697-67-7P  
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT  
 (Reactant or reagent)  
 (starting material; prepn. of biaryl phosphine and amine ligands for

improved palladium-catalyzed amination reactions, Suzuki couplings, arylations, vinylations, and carbon-oxygen bond formation reactions)  
IT 251320-80-6P, N-(Diphenylmethylene)-2-bromoaniline  
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)  
(synthetic product; prepn. of biaryl phosphine and amine ligands for improved palladium-catalyzed amination reactions, Suzuki couplings, arylations, vinylations, and carbon-oxygen bond formation reactions)  
IT 86-26-0P 92-69-3P, 4-Hydroxybiphenyl 92-91-1P, 4-Acetyl biphenyl 92-93-3P, 4-Nitrobiphenyl 101-70-2P, 4,4'-Dimethoxydiphenylamine 121-00-6P 613-37-6P, 4-Methoxybiphenyl 620-83-7P 620-93-9P, Di-p-tolylamine 644-08-6P, 4-Methylbiphenyl 720-75-2P, Methyl 4-phenylbenzoate 730-11-0P, 4-Methoxy-4'-nitrodiphenylamine 774-52-7P, N-(4-Methylphenyl)piperidine 825-54-7P 825-55-8P, 2-Phenylthiophene 1208-86-2P 1625-92-9P, 4-t-Butylbiphenyl 2142-66-7P, 2-Acetyl biphenyl 2920-38-9P, 4-Cyanobiphenyl 2928-43-0P, 2-(Hydroxymethyl)biphenyl 3077-16-5P, N-(4-Methylphenyl)morpholine 3470-65-3P 3976-34-9P, 2,6-Dimethylbiphenyl 4036-43-5P 4075-79-0P, N-Acetyl-4-aminobiphenyl 4316-51-2P, N-(4-Methoxyphenyl)-N,N-diphenylamine 4316-53-4P 4496-49-5P 4787-76-2P, N-(2-Methoxyphenyl)pyrrolidine 5031-78-7P 5405-15-2P, N-Benzyl-p-toluidine 5405-19-6P 6574-15-8P, N-(4-Nitrophenyl)piperidine 6935-27-9P, N-Benzyl-2-aminopyridine 7372-85-2P, 2,5-Dimethylbiphenyl 10273-87-7P 10282-31-2P, N-(4-Cyanophenyl)morpholine 15359-99-6P 15360-00-6P 16251-99-3P 16819-50-4P, N-(2,6-Dimethylphenyl)benzylamine 17057-88-4P, 3,5-Dimethylbiphenyl 17952-07-7P 19853-10-2P, [1,1'-Biphenyl]-2-acetonitrile 21218-94-0P 23600-89-7P 23676-05-3P 23699-65-2P, N-(3-Acetylphenyl)aniline 23951-29-3P 24255-25-2P, N-(2-Pyridyl)morpholine 25539-14-4P 25699-92-7P, N-(4-Cyanophenyl)indole 25700-23-6P, N-(3-Pyridyl)indole 27347-14-4P 31144-33-9P 31603-95-9P, 4-tert-Butyl-1-tert-butyloxybenzene 34160-16-2P 35393-20-5P, N-(Diphenylmethylene)-4-nitroaniline 38158-65-5P 38869-05-5P 39253-43-5P 39910-98-0P, N-(4-Acetylphenyl)morpholine 50798-94-2P, N-(2-Methoxyphenyl)benzylamine 50910-08-2P, N-(2-Pyridyl)-N,N-diphenylamine 51580-77-9P 51786-49-3P 52351-44-7P, N-(4-Methoxyphenyl)-2-phenylindole 54480-44-3P, 4-Methoxy-4'-(dimethylamino)diphenylamine 54660-04-7P, N-(4-Methoxyphenyl)pyrrolidine 55251-46-2P 56052-33-6P 56506-60-6P, N-(4-Methylphenyl)hexylamine 56915-80-1P, 1-(3-Acetylphenyl)-4-methylpiperazine 60893-66-5P 61394-81-8P 62787-14-8P 62787-15-9P 62790-83-4P 62790-85-6P 68856-26-8P 70945-85-6P 75201-55-7P 75934-30-4P 76650-29-8P, 4-Acetyl-3'-methylbiphenyl 76708-72-0P 76708-78-6P, 2,5,3'-Trimethylbiphenyl 77422-28-7P 81693-80-3P, 4-Hexylanisole 82749-62-0P 83188-35-6P 84736-47-0P, N-(4-t-Butylphenyl)morpholine 84736-54-9P, 2-(4-Methoxyphenyl)-3-pentanone 84839-92-9P 84839-93-0P 91949-95-0P, 4-Isopropoxybenzonitrile 92495-53-9P, 4-Methyl-2'-methoxybiphenyl 92670-29-6P, N-(3-Pyridyl)morpholine 93597-01-4P, N-(4-Methoxyphenyl)indole 94540-42-8P 94959-58-7P 97053-04-8P 97413-60-0P 114081-08-2P 114772-53-1P 116267-90-4P, N-(3-Thiophenyl)-N,N-diphenylamine 123324-87-8P 124043-95-4P 129644-26-4P 137445-01-3P 138900-16-0P, N-(4-Fluorophenyl)indole 138900-19-3P 146803-96-5P 167283-32-1P, N-(4-Methylphenyl)indole 171092-38-9P, 3-(3-Acetylphenyl)pyridine 172878-95-4P 174307-96-1P 175696-73-8P, N-(3-Cyanophenyl)pyrrolidine 179487-70-8P 180336-54-3P, N-(2,5-Dimethylphenyl)-N-methylaniline 183135-51-5P, N-Methyl-N-(3-pyridyl)aniline 183135-52-6P 185259-34-1P, N-(4-t-Butylphenyl)piperidine 188026-55-3P, N,N-Dibutyl-4-t-butylaniline 188026-64-4P, N-Ethyl-N-(3,5-dimethylphenyl)aniline 188026-74-6P 196604-19-0P 196604-21-4P 196604-24-7P 197172-67-1P 197172-69-3P 197640-99-6P 202802-70-8P 211292-60-3P 211292-66-9P, 2,6-Diisopropyl-2',6'-dimethyldiphenylamine 212382-74-6P 213014-13-2P 213697-51-9P 213697-52-0P, 2,6-Dimethyl-N-hexylaniline 213697-65-5P,

1,1-Bis(4-methylphenyl)-3-methyl-2-butanone 213697-66-6P 215394-88-0P  
 223248-27-9P 223655-23-0P 224311-62-0P 224311-63-1P 224311-65-3P  
 224311-66-4P 224311-67-5P 224311-68-6P 224311-69-7P 224311-70-0P  
 224311-72-2P 224311-73-3P 224311-74-4P 224311-75-5P 224311-76-6P  
 226569-78-4P 226917-75-5P, N-(4-Cyanophenyl)hexylamine 247940-07-4P,  
 N-Methyl-N-(3,5-dimethoxyphenyl)aniline 247940-08-5P 251320-76-0P  
 251320-77-1P, 4-Formyl-4'-ethoxybiphenyl 251320-78-2P 251320-79-3P  
 251320-81-7P, 3-Acetyl-3',5'-dimethoxybiphenyl 251320-82-8P  
 251320-83-9P 251320-84-0P, 2-Methoxy-2'-acetyl biphenyl 253768-96-6P,  
 N-(3-Cyanophenyl)benzylamine 255835-86-0P 255835-87-1P 255835-88-2P  
 255835-89-3P 255835-90-6P 255835-91-7P, N-(2,6-  
 Dimethylphenyl)morpholine 255835-92-8P 255835-93-9P,  
 N-(4-t-Butylphenyl)benzylamine 255835-94-0P, N-(3,4-  
 Dimethylphenyl)pyrrolidine 255835-95-1P, 2-Methoxy-4'-cyanodiphenylamine  
 255835-96-2P 255835-97-3P 255835-98-4P 255835-99-5P 255836-00-1P  
 255836-01-2P 255836-02-3P 255836-04-5P, N-(2-Methoxyphenyl)-N-(3-  
 methoxyphenyl)-N-(4-methoxyphenyl)amine 255836-06-7P,  
 N-(4-Dimethylaminophenyl)-N-(4-methoxyphenyl)-N-(3-methylphenyl)amine  
 255836-08-9P, N-(2,4-Dimethylphenyl)-N-(4-methoxyphenyl)-N-(3-  
 methylphenyl)amine 255836-10-3P 255836-12-5P 255836-14-7P,  
 N-(4-Butylphenyl)-N-(4-methoxyphenyl)-N-(4-methylphenyl)amine  
 255836-15-8P, N-(2,5-Dimethylphenyl)-N-(3,5-dimethylphenyl)-N-(4-  
 methylphenyl)amine 255836-17-0P 255836-19-2P, N-(4-tert-  
 Butylphenyl)indole 255836-21-6P 255836-23-8P, N-Cyclopropyl-4-tert-  
 butylaniline 255836-25-0P, N-Cyclopropyl-2,5-dimethylaniline  
 255836-28-3P 255836-30-7P 255836-36-3P 255836-38-5P 255836-39-6P  
 255836-41-0P 255836-43-2P 255836-44-3P 255836-45-4P,  
 2-Methyl-4-(4-butylphenyl)-3-pentanone 255836-46-5P 255836-48-7P  
 255836-50-1P 255836-52-3P 255836-54-5P, 2-(3-Hydroxyphenyl)-3-  
 pentanone 255836-56-7P, 2,4-Dimethyl-2-(4-t-butylphenyl)-3-pentanone  
 255836-57-8P 255836-59-0P 255836-61-4P 255836-63-6P 255836-70-5P,  
 N-(4-t-Butylphenyl)-2-phenylindole 255836-72-7P 255836-74-9P,  
 N-(3,5-Dimethylphenyl)-2,3-dimethylindole 255836-76-1P,  
 N-(4-t-Butylphenyl)-2,3,7-trimethylindole 255836-78-3P 255836-80-7P,  
 N-(2-Pyridyl)-7-ethylindole 255836-82-9P, N-(3,5-Dimethylphenyl)-7-  
 ethylindole 255836-84-1P 255836-86-3P 255836-88-5P 255836-90-9P  
 255836-92-1P 255836-94-3P 255836-95-4P 255836-96-5P 255836-97-6P  
 255836-98-7P 255836-99-8P 255837-00-4P 255837-01-5P 255837-02-6P  
 255837-03-7P

RL: SPN (Synthetic preparation); PREP (Preparation)  
 (synthetic product; prepn. of biaryl phosphine and amine ligands for  
 improved palladium-catalyzed amination reactions, Suzuki couplings,  
 arylations, vinylations, and carbon-oxygen bond formation reactions)

IT 255837-04-8P 255837-05-9P 255837-06-0P 255837-07-1P 255837-08-2P  
 255837-09-3P 255837-10-6P 255837-11-7P 255837-12-8P 255837-13-9P

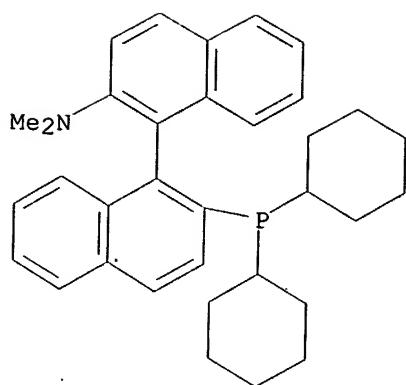
RL: SPN (Synthetic preparation); PREP (Preparation)  
 (synthetic product; prepn. of biaryl phosphine and amine ligands for  
 improved palladium-catalyzed amination reactions, Suzuki couplings,  
 arylations, vinylations, and carbon-oxygen bond formation reactions)

IT 255882-15-6 255882-16-7

RL: CAT (Catalyst use); USES (Uses)  
 (catalyst; prepn. of biaryl phosphine and amine ligands for improved  
 palladium-catalyzed amination reactions, Suzuki couplings, arylations,  
 vinylations, and carbon-oxygen bond formation reactions)

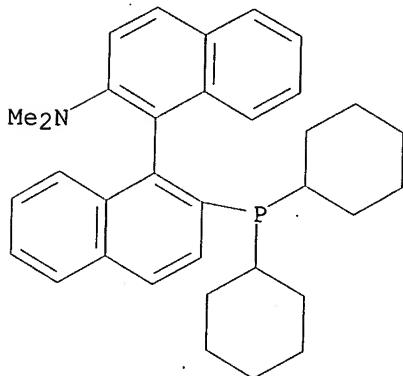
RN 255882-15-6 HCPLUS

CN [1,1'-Binaphthalen]-2-amine, 2'-(dicyclohexylphosphino)-N,N-dimethyl-,  
 (R)- (9CI) (CA INDEX NAME)



RN 255882-16-7 HCPLUS

CN [1,1'-Binaphthalen]-2-amine, 2'-(dicyclohexylphosphino)-N,N-dimethyl-,  
(S)- (9CI) (CA INDEX NAME)



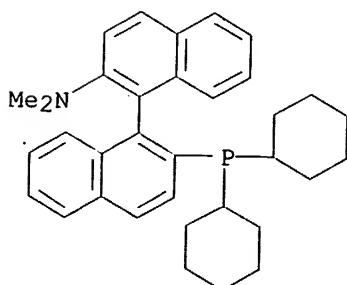
IT 255835-81-5P

RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation);  
USES (Uses)

(prepd. catalyst; prepn. of biaryl phosphine and amine ligands for  
improved palladium-catalyzed amination reactions, Suzuki couplings,  
arylations, vinylations, and carbon-oxygen bond formation reactions)

RN 255835-81-5 HCPLUS

CN [1,1'-Binaphthalen]-2-amine, 2'-(dicyclohexylphosphino)-N,N-dimethyl-  
(9CI) (CA INDEX NAME)



=> fil reg  
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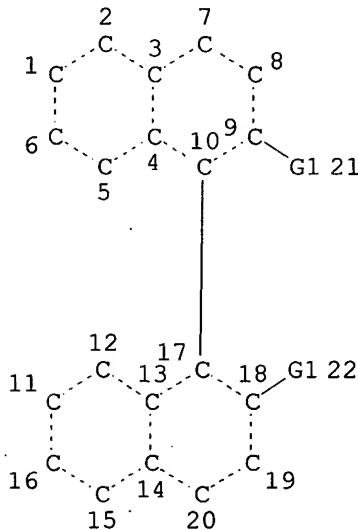
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Experimental and calculated property data are now available. See HELP PROPERTIES for more information. See STNote 27, Searching Properties in the CAS Registry File, for complete details:  
<http://www.cas.org/ONLINE/STN/STNOTES/stnotes27.pdf>

=> d sta que 121  
L19 STR



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VAR G1=N/P/AS/O/S  
NODE ATTRIBUTES:  
DEFAULT MLEVEL IS ATOM  
DEFAULT ECLEVEL IS LIMITED

GRAPH ATTRIBUTES:  
RING(S) ARE ISOLATED OR EMBEDDED  
NUMBER OF NODES IS 22

STEREO ATTRIBUTES: NONE  
L21 6721 SEA FILE=REGISTRY SSS FUL L19

100.0% PROCESSED 12141 ITERATIONS  
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6721 ANSWERS

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L21 (FILE 'REGISTRY' ENTERED AT 08:54:49 ON 12 MAY 2003)  
 6721 S L19 FUL

L22 SAV TEMP L21 SACKEY004/A  
 6718 S L21 NOT L11

L23 .7 S L22 AND L10

L24 5728 S L22 NOT (PMS OR CCS OR MNS)/CI

L25 FILE 'HCAPLUS' ENTERED AT 08:59:36 ON 12 MAY 2003  
 4102 S L22

L26 44 S L1-L9 AND L25  
 SEL HIT RN

L27 FILE 'REGISTRY' ENTERED AT 09:00:08 ON 12 MAY 2003  
 50 S E490-E539

L28 FILE 'HCAPLUS' ENTERED AT 09:01:02 ON 12 MAY 2003  
 2247 S L27

L29 44 S L26 AND L28

L30 22 S L29 AND (PY<=1998 OR PRY<=1998 OR AY<=1998)  
 7 S L30 AND ORGANOMETAL?/SC,SX

L31 35 S L27 (L) CAT/RL AND L29

L32 15 S L30 AND L32

L33 19 S L31,L33

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 FILE LAST UPDATED: 11 May 2003 (20030511/ED)

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L34 ANSWER 1 OF 19 HCAPLUS COPYRIGHT 2003 ACS  
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DN 135:318588

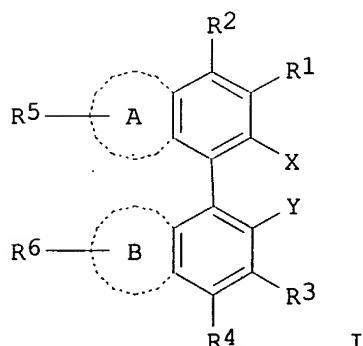
TI Biaryl phosphine and amine ligands for improved transition metal-catalyzed processes

IN Buchwald, Stephen L.; Old, David W.; Wolfe, John P.; Palucki, Michael; Kamikawa, Ken

PA Massachusetts Institute of Technology, USA  
 SO U.S., 55 pp., Cont.-in-part of U.S. Ser. No. 113,478.  
 CODEN: USXXAM  
 DT Patent  
 LA English  
 IC ICM C07C255-03  
 ICS C07F009-28; C07D265-30; C07D211-70; C07D209-04  
 NCL 558388000  
 CC 29-7 (Organometallic and Organometalloidal Compounds)  
 Section cross-reference(s): 25

## FAN.CNT 2

|      | PATENT NO.   | KIND | DATE     | APPLICATION NO. | DATE         |
|------|--|------|----------|-----------------|--------------|
| PI   | US 6307087   | B1   | 20011023 | US 1999-231315  | 19990113 <-- |
|      | US 6395916   | B1   | 20020528 | US 1998-113478  | 19980710 <-- |
|      | CA 2336691   | AA   | 20000120 | CA 1999-2336691 | 19990709 <-- |
|      | WO 2000002887  | A2   | 20000120 | WO 1999-US15450 | 19990709 <-- |
|      | WO 2000002887  | A3   | 20000629 |                 |              |
|      | W: CA, JP  |      |          |                 |              |
|      | RW: AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE |      |          |                 |              |
|      | EP 1097158   | A2   | 20010509 | EP 1999-933785  | 19990709 <-- |
|      | R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, FI  |      |          |                 |              |
|      | JP 2002520328  | T2   | 20020709 | JP 2000-559117  | 19990709 <-- |
|      | US 2002156295  | A1   | 20021024 | US 2001-4101    | 20011023 <-- |
| PRAI | US 1998-113478   | A2   | 19980710 | <--             |              |
|      | US 1998-196855   | A    | 19981120 | <--             |              |
|      | US 1999-231315   | A    | 19990113 |                 |              |
|      | US 1999-239024   | A    | 19990127 |                 |              |
|      | WO 1999-US15450  | W    | 19990709 | <--             |              |
| OS   | CASREACT 135:318588; MARPAT 135:318588                                     |      |          |                 |              |
| GI   |  |      |          |                 |              |



AB The present invention relates to the prepn. of novel biaryl phosphine and amine ligands (I) [wherein A and B = independently fused monocyclic or polycyclic cycloalkyl, cycloalkenyl, aryl, or heterocyclic rings of 4-8 atoms; X = NR<sub>2</sub>, PR<sub>2</sub>, AsR<sub>2</sub>, OR, or SR; Y = NR<sub>2</sub>, PR<sub>2</sub>, AsR<sub>2</sub>, OR, SR, SiR<sub>3</sub>, alkyl, or H; R-R<sub>6</sub> = independently H, halogen, (hetero)alkyl, alkenyl, alkynyl, hydroxy, alkoxy, silyloxy, amino, nitro, sulphydryl, amide, carbonyl, ketone, anhydride, silyl, thioalkyl, ketone, ester, nitrile, (hetero)aryl, etc.] for transition metals and their use in metal-catalyzed carbon-heteroatom and carbon-carbon bond-forming reactions. Unexpected improvements over the prior art were demonstrated in transition metal-catalyzed aryl amination reactions, Suzuki couplings giving both biaryl and alkylaryl products, arylation and vinylations at the position

.alpha. to carbonyl groups, and carbon-oxygen bond formation. The ligands and methods of the invention enable transformations utilizing aryl chlorides and bromides at room temp. at synthetically useful rates with extremely small amts. of catalyst relative to the limiting reagent. For example, coupling of p-chlorobenzonitrile and morpholine was catalyzed by 2.5 mol% Pd2(dbu)3, 7.5 mol% of 2-(N,N-dimethylamino)-2'-  
(dicyclohexylphosphino)biphenyl, and NaOBu-t in DME at room temp. to provide 4-(4-morpholinyl)benzonitrile in 96% yield. Thus, the subject processes provide improvements in many features of the transition metal-catalyzed reactions, including the range of suitable substrates, reaction conditions, and efficiency.

ST biaryl phosphine amine ligand prepn transition metal catalyst; amination aryl chloride bromide palladium catalysts; Suzuki coupling aryl chloride bromide palladium catalysts; ketone arylation palladium catalysts

IT Amines, preparation  
RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation); USES (Uses)  
(arom.; biaryl phosphine and amine ligands for improved transition metal-catalyzed processes)

IT Ketones, preparation  
RL: SPN (Synthetic preparation); PREP (Preparation)  
(arom.; biaryl phosphine and amine ligands for improved transition metal-catalyzed processes)

IT Aryl halides  
RL: RCT (Reactant); RACT (Reactant or reagent)  
(aryl chlorides; biaryl phosphine and amine ligands for improved transition metal-catalyzed processes)

IT Chlorides, reactions  
RL: RCT (Reactant); RACT (Reactant or reagent)  
(aryl; biaryl phosphine and amine ligands for improved transition metal-catalyzed processes)

IT Amination  
Amination catalysts  
Arylation  
Arylation catalysts  
Cross-coupling reaction catalysts  
Suzuki coupling reaction  
(biaryl phosphine and amine ligands for improved transition metal-catalyzed processes)

IT Phosphines  
RL: CAT (Catalyst use); USES (Uses)  
(biaryl phosphine and amine ligands for improved transition metal-catalyzed processes)

IT Biaryls  
RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation); USES (Uses)  
(biaryl phosphine and amine ligands for improved transition metal-catalyzed processes)

IT Aryl bromides  
RL: RCT (Reactant); RACT (Reactant or reagent)  
(biaryl phosphine and amine ligands for improved transition metal-catalyzed processes)

IT Transition metal complexes  
RL: CAT (Catalyst use); USES (Uses)  
(phosphine; biaryl phosphine and amine ligands for improved transition metal-catalyzed processes)

IT Phosphines  
RL: CAT (Catalyst use); USES (Uses)  
(transition metal complexes; biaryl phosphine and amine ligands for improved transition metal-catalyzed processes)

IT 127-09-3, Sodium acetate 534-17-8 584-08-7, Potassium carbonate 3375-31-3, Palladium diacetate 6476-37-5, Dicyclohexylphenylphosphine 7778-53-2 7789-23-3, Potassium fluoride 13400-13-0, Cesium fluoride

14221-01-3, Tetrakis(triphenylphosphine)palladium 51364-51-3,  
 Tris(dibenzylideneacetone)dipalladium 54000-83-8, 2,6-Dimethoxyphenyl-di-t-butylphosphine 166330-10-5 213774-71-1 255837-14-0,  
 2,4,6-Trimethoxyphenyl-di-t-butylphosphine  
 RL: CAT (Catalyst use); USES (Uses)  
 (biaryl phosphine and amine ligands for improved transition metal-catalyzed processes)

IT 213697-53-1P 224311-51-7P, 2-(Di-tert-butylphosphino)biphenyl  
 255835-81-5P 255835-82-6P  
 RL: CAT (Catalyst use); IMF (Industrial manufacture); SPN (Synthetic preparation); PREP (Preparation); USES (Uses)  
 (biaryl phosphine and amine ligands for improved transition metal-catalyzed processes)

IT 4688-76-0P 20837-12-1P 59734-92-8P 75295-57-7P 89291-23-6P  
 128796-39-4P, 4-(Trifluoromethyl)phenylboronic acid 157282-19-4P  
 213697-67-7P 224311-57-3P 224311-58-4P 224311-59-5P 255837-15-1P,  
 2-Bromo-4'(trifluoromethyl)biphenyl 255837-16-2P  
 RL: IMF (Industrial manufacture); RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)  
 (biaryl phosphine and amine ligands for improved transition metal-catalyzed processes)

IT 92-69-3P, 4-Hydroxybiphenyl 92-91-1P, 4-Acetyl biphenyl 92-93-3P,  
 4-Nitrobiphenyl 612-75-9P, 3,3'-Dimethylbiphenyl 613-37-6P 644-08-6P  
 720-75-2P 825-55-8P, 2-Phenylthiophene 2142-66-7P, 2-Acetyl biphenyl  
 2920-38-9P, 4-Cyanobiphenyl 2928-43-0P, 2-Hydroxymethylbiphenyl  
 3976-34-9P, 2,6-Dimethylbiphenyl 4075-79-0P, n-Acetyl-4-aminobiphenyl  
 5405-15-2P 7372-85-2P, 2,5-Dimethylbiphenyl 10282-31-2P 17057-88-4P  
 19853-10-2P, [1,1'-Biphenyl]-2-acetonitrile 23676-05-3P 31144-33-9P  
 39253-43-5P 39910-98-0P, n-(4-Acetylphenyl)morpholine 54660-04-7P,  
 n-(4-Methoxyphenyl)pyrrolidine 76650-29-8P 76708-78-6P 81693-80-3P  
 82749-62-0P 92495-53-9P 138900-16-0P, N-(4-Fluorophenyl)indole  
 167283-32-1P, N-(4-Methylphenyl)indole 171092-38-9P,  
 3-(3-Acetylphenyl)pyridine 174307-96-1P 180336-54-3P,  
 N-(2,5-Dimethylphenyl)-N-methylaniline 197172-67-1P 213697-51-9P,  
 n-(2,5-Dimethylphenyl)morpholine 213697-52-0P 213697-65-5P  
 213697-66-6P 224311-54-0P 224311-55-1P 251320-77-1P 251320-78-2P  
 251320-81-7P, 3-Acetyl-3',5'-dimethoxybiphenyl 251320-82-8P,  
 4-Carbomethoxy-3'-acetyl biphenyl 251320-84-0P 255835-83-7P,  
 2-(Di-t-butylphosphino)-4'-(trifluoromethyl)biphenyl 255835-84-8P  
 255835-85-9P 255882-14-5P  
 RL: IMF (Industrial manufacture); SPN (Synthetic preparation); PREP (Preparation)  
 (biaryl phosphine and amine ligands for improved transition metal-catalyzed processes)

IT 95-72-7 98-80-6 99-90-1 99-91-2 100-00-5, 1-Chloro-4-nitrobenzene  
 100-46-9, Benzylamine, reactions 100-61-8, n-Methylaniline, reactions  
 103-88-8, 4'-Bromoacetanilide 106-38-7 106-41-2, 4-Bromophenol  
 106-43-4 106-49-0, p-Toluidine, reactions 108-94-1, Cyclohexanone,  
 reactions 110-91-8, Morpholine, reactions 111-26-2, Hexylamine  
 111-92-2, Dibutylamine 120-72-9, Indole, reactions 123-75-1,  
 Pyrrolidine, reactions 402-43-7, 4-(Trifluoromethyl)phenyl bromide  
 460-00-4, 1-Bromo-4-fluorobenzene 553-94-6, 2-Bromo-p-xylene 556-96-7  
 563-80-4 565-69-5 576-22-7 583-53-9, 1,2-Dibromobenzene 583-55-1,  
 2-Bromoiodobenzene 592-41-6, 1-Hexene, reactions 619-42-1 623-03-0,  
 4-Chlorobenzonitrile 623-12-1 626-60-8, 3-Chloropyridine 698-00-0  
 768-90-1, 1-Bromoadamantane 1003-09-4, 2-Bromothiophene 1013-88-3,  
 Benzophenone imine 1079-66-9, Chlorodiphenylphosphine 1122-91-4,  
 4-Bromobenzaldehyde 1126-46-1 2052-07-5, 2-Bromobiphenyl 2142-68-9,  
 2'-Chloroacetophenone 2856-63-5, 2-Chlorobenzyl cyanide 3972-65-4,  
 1-Bromo-4-t-butylbenzene 5720-06-9 7051-16-3 13716-10-4,  
 Chlorodi-tert-butylphosphine 16523-54-9, Chlorodiclohexylphosphine  
 17933-03-8 18982-54-2, 2-Bromobenzylalcohol 22237-13-4,  
 4-Ethoxyphenylboronic acid 40138-16-7 42371-64-2 53847-33-9

74866-28-7, 2,2'-Dibromo-1,1'-binaphthyl 204841-19-0, 3-Acetylphenyl  
 boronic acid 251320-89-5, 2-(Bromo)-2'-(isopropyl)biphenyl  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (biaryl phosphine and amine ligands for improved transition  
 metal-catalyzed processes)

RE.CNT 131 THERE ARE 131 CITED REFERENCES AVAILABLE FOR THIS RECORD  
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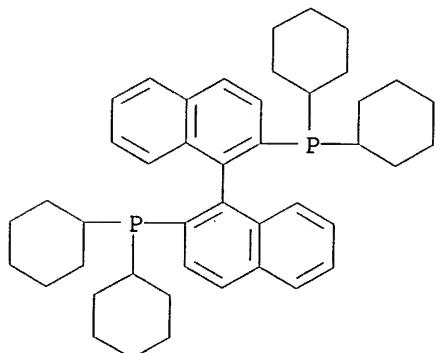
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 (119) Vyskocil, S; Am Chem Soc, Newsletter and Abstracts, 216th ACS National Meeting 1998, 538  
 (120) Wang, D; Chem Commun 1999, P529 HCPLUS  
 (121) Wolfe, J; J Am Chem Soc 1996, V118, P7215 HCPLUS  
 (122) Wolfe, P; Angewandte Chemie International Edition 1999, V38(16), P2413  
 (123) Wolfe, P; J Am Chem Soc 1999, V121(41), P9550  
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 (125) Yamamoto; US 5268492 1993 HCPLUS  
 (126) Yamamoto, T; Tetrahedron Letters 1998, V39, P2367 HCPLUS  
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 (128) Zhang; US 5767276 1998 HCPLUS  
 (129) Zhang; Tetrahedron Letters 1991, V32(49), P7283 HCPLUS  
 (130) Zhao; US 5508458 1996 HCPLUS  
 (131) Zhao; Tetrahedron Letters 1996, V37(26), P4463 HCPLUS

IT 213774-71-1

RL: CAT (Catalyst use); USES (Uses)  
 (biaryl phosphine and amine ligands for improved transition metal-catalyzed processes)

RN 213774-71-1 HCPLUS

CN Phosphine, [1,1'-binaphthalene]-2,2'-diylbis[dicyclohexyl- (9CI) (CA INDEX NAME)]

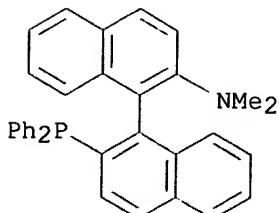


IT 255882-14-5P

RL: IMF (Industrial manufacture); SPN (Synthetic preparation); PREP (Preparation)  
 (biaryl phosphine and amine ligands for improved transition metal-catalyzed processes)

RN 255882-14-5 HCPLUS

CN [1,1'-Binaphthalen]-2-amine, 2'-(diphenylphosphino)-N,N-dimethyl- (9CI) (CA INDEX NAME)



DN 132:107774  
 TI Transition metal catalyzed amination of aryl halides and triflates using imines.

IN Wolfe, John P.; Ahman, Jens; Sadighi, Joseph P.; Singer, Robert A.; Buchwald, Stephen L.

PA Massachusetts Institute of Technology, USA  
 SO PCT Int. Appl., 61 pp.

CODEN: PIXXD2

DT Patent

LA English

IC ICM C07C249-02

ICS C07C251-04

CC 25-4 (Benzene, Its Derivatives, and Condensed Benzenoid Compounds)  
 Section cross-reference(s): 27, 67

FAN.CNT 1

| PATENT NO.   | KIND | DATE     | APPLICATION NO. | DATE         |
|--|------|----------|-----------------|--------------|
| WO 2000005199  | A1   | 20000203 | WO 1999-US16257 | 19990723 <-- |
| W: CA, JP  |      |          |                 |              |
| RW: AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE |      |          |                 |              |
| US 6323366   | B1   | 20011127 | US 1998-122324  | 19980724 <-- |
| CA 2336976   | AA   | 20000203 | CA 1999-2336976 | 19990723 <-- |
| EP 1100774   | A1   | 20010523 | EP 1999-937293  | 19990723 <-- |
| R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, FI  |      |          |                 |              |
| JP 2002521359  | T2   | 20020716 | JP 2000-561156  | 19990723 <-- |

PRAI US 1998-122324 A 19980724 <--  
 US 1997-54092P P 19970729 <--  
 WO 1999-US16257 W 19990723

OS CASREACT 132:107774; MARPAT 132:107774

AB ArN:CR1R2 [Ar = (substituted) (hetero)aryl; R1, R2 = H, (substituted) alkyl, alkenyl, alkynyl, (hetero)aryl, (hetero)arylkylalkyl, etc.; R1R2 = atoms to form a (substituted) ring], were prep'd. by reaction of ArX (X = Cl, Br, iodo, OSO<sub>2</sub>X<sub>1</sub>, OSO<sub>2</sub>A, OSO<sub>2</sub>Ar; A = alkyl, X<sub>1</sub> = halo) with RN:CR1R2 [R = H, trialkylstannyl, triarylstannyl, trialkylsilyl, triarylsilyl, Li, Na, K, Mg halide, Ca halide, Zn halide, B(OH)<sub>2</sub>, groups replaced by H under the reaction conditions] in the presence of a transition metal catalyst selected from groups 5-12 (Ni excepted) of the periodic table and a base selected from alkoxides, aryloxides, carbonates, amides, phosphates, and fluorides. Thus, Pd(OAc)<sub>2</sub>, bis(2-diphenylphosphino)phenyl ether, benzophenone imine, and 4-BrC<sub>6</sub>H<sub>4</sub>CMe<sub>3</sub> were stirred in PhMe; NaOCMe<sub>3</sub> was added and the mixt. was heated to 80.degree. to give 90% N-diphenylmethylene-4-tert-butylaniline.

ST aryl halide triflate imination transition metal catalyst imine; imine arom prep'n

IT Amines, preparation

RL: SPN (Synthetic preparation); PREP (Preparation)  
 (arom.; transition metal catalyzed amination of aryl halides and triflates using imines)

IT Imination

Imination  
 (catalysts; transition metal catalyzed amination of aryl halides and triflates using imines)

IT Catalysts

Catalysts  
 (imination catalysts; transition metal catalyzed amination of aryl halides and triflates using imines)

IT Imination

(transition metal catalyzed amination of aryl halides and triflates using imines)

IT Transition metals, uses

RL: CAT (Catalyst use); USES (Uses)

(transition metal catalyzed amination of aryl halides and triflates using imines)

IT Imines  
 RL: IMF (Industrial manufacture); SPN (Synthetic preparation); PREP (Preparation)  
 (transition metal catalyzed amination of aryl halides and triflates using imines)

IT Carbonates, miscellaneous  
 Metal alkoxides  
 RL: MSC (Miscellaneous)  
 (transition metal catalyzed amination of aryl halides and triflates using imines)

IT 3375-31-3, Palladium diacetate 7440-05-3, Palladium, uses 12150-46-8,  
 DPPF 51364-51-3, Tris(dibenzylideneacetone)dipalladium  
 98327-87-8, BINAP 166330-10-5 255897-36-0  
 RL: CAT (Catalyst use); USES (Uses)  
 (transition metal catalyzed amination of aryl halides and triflates using imines)

IT 32566-86-2P 197144-29-9P 197144-30-2P  
 RL: IMF (Industrial manufacture); RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)  
 (transition metal catalyzed amination of aryl halides and triflates using imines)

IT 17273-16-4P, N-Diphenylmethylene-4-chloroaniline 35393-20-5P,  
 N-Diphenylmethylene-4-nitroaniline 42834-19-5P, N-Diphenylmethylene-4-methoxyaniline 53847-32-8P, N-Diphenylmethylene-2-chloroaniline 73939-13-6P, N-Diphenylmethylene-2-methoxyaniline 197144-28-8P,  
 N-Diphenylmethylene-4-tert-butylaniline 255835-90-6P,  
 N-Diphenylmethylene-3,5-dimethoxyaniline 255897-33-7P 255897-34-8P,  
 N-Diphenylmethylene-3-(1,3-dioxolan-2-yl)aniline 255897-35-9P,  
 N-Diphenylmethylene-3-fluoroaniline  
 RL: IMF (Industrial manufacture); SPN (Synthetic preparation); PREP (Preparation)  
 (transition metal catalyzed amination of aryl halides and triflates using imines)

IT 534-17-8, Cesium carbonate 865-48-5  
 RL: MSC (Miscellaneous)  
 (transition metal catalyzed amination of aryl halides and triflates using imines)

IT 100-00-5, 1-Chloro-4-nitrobenzene 104-92-7, 4-Bromoanisole 106-39-8,  
 4-Bromochlorobenzene 553-94-6, 2,5-Dimethylbromobenzene 578-57-4,  
 2-Bromoanisole 589-87-7, 4-Bromoiodobenzene 619-42-1 623-00-7  
 626-60-8, 3-Chloropyridine 694-80-4, 2-Bromochlorobenzene 696-62-8,  
 4-Methoxyiodobenzene 1013-88-3 1073-06-9, 3-Bromofluorobenzene  
 2398-37-0, 3-Bromoanisole 3972-65-4, 1-Bromo-4-tert-butylbenzene  
 7051-16-3, 3,5-Dimethoxychlorobenzene 17763-71-2 17789-14-9,  
 2-(3-Bromophenyl)-1,3-dioxolane 60876-70-2, 4-tert-Butoxybromobenzene  
 66107-32-2 99747-74-7 107658-28-6 109613-00-5 197144-27-7  
 255901-58-7  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (transition metal catalyzed amination of aryl halides and triflates using imines)

IT 90-04-0P, 2-Methoxyaniline 95-78-3P, 2,5-Dimethylaniline 99-92-3P,  
 4-Acylaniline 104-94-9P, 4-Methoxyaniline 106-40-1P, 4-Bromoaniline  
 134-32-7P, 1-Aminonaphthalene 462-08-8P, 3-Aminopyridine 619-45-4P,  
 4-Methoxycarbonylaniline 769-92-6P, 4-tert-Butylaniline 873-74-5P,  
 4-Cyanoaniline 4518-10-9P, 3-Methoxycarbonylaniline 6398-87-4P  
 197144-31-3P 255901-57-6P  
 RL: SPN (Synthetic preparation); PREP (Preparation)  
 (transition metal catalyzed amination of aryl halides and triflates using imines)

RE.CNT 3 THERE ARE 3 CITED REFERENCES AVAILABLE FOR THIS RECORD  
 RE

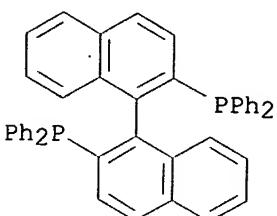
(1) Daicel Chem Ind Ltd; JP 09239275 A 1997 HCPLUS  
 (2) Institut Francais Du Petrole; FR 2474491 A 1981 HCPLUS  
 (3) Syntex Corporation; GB 1047925 A 1966

IT 98327-87-8, BINAP

RL: CAT (Catalyst use); USES (Uses)  
 (transition metal catalyzed amination of aryl halides and triflates  
 using imines)

RN 98327-87-8 HCPLUS

CN Phosphine, [1,1'-binaphthalene]-2,2'-diylbis[diphenyl- (9CI) (CA INDEX  
 NAME)]

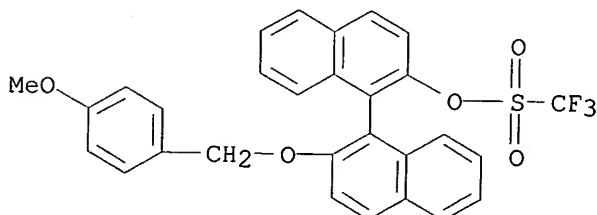


IT 255901-58-7

RL: RCT (Reactant); RACT (Reactant or reagent)  
 (transition metal catalyzed amination of aryl halides and triflates  
 using imines)

RN 255901-58-7 HCPLUS

CN Methanesulfonic acid, trifluoro-, 2'-[(4-methoxyphenyl)methoxy][1,1'-binaphthalen]-2-yl ester (9CI) (CA INDEX NAME)

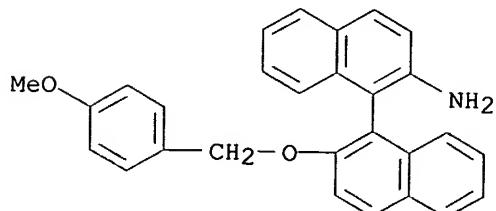


IT 255901-57-6P

RL: SPN (Synthetic preparation); PREP (Preparation)  
 (transition metal catalyzed amination of aryl halides and triflates  
 using imines)

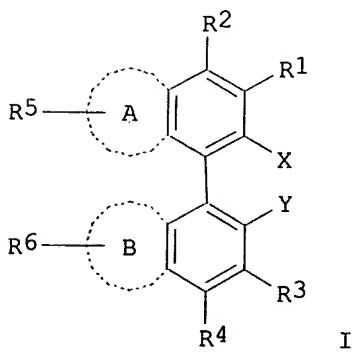
RN 255901-57-6 HCPLUS

CN [1,1'-Binaphthalen]-2-amine, 2'-[(4-methoxyphenyl)methoxy]- (9CI) (CA INDEX NAME)



DN 132:108101  
 TI Biaryl phosphine and amine ligands for improved transition metal-catalyzed processes  
 IN Buchwald, Stephen; Old, David W.; Wolfe, John P.; Palucki, Michael; Kamikawa, Ken; Chieffi, Andrew; Sadighi, Joseph P.; Singer, Robert A.; Ahman, Jens  
 PA Massachusetts Institute of Technology, USA  
 SO PCT Int. Appl., 397 pp.  
 CODEN: PIXXD2  
 DT Patent  
 LA English  
 IC ICM C07F009-02  
 CC 29-7 (Organometallic and Organometalloidal Compounds)  
 Section cross-reference(s): 25  
 FAN.CNT 2

|      | PATENT NO.   | KIND | DATE     | APPLICATION NO. | DATE         |
|------|--|------|----------|-----------------|--------------|
| PI   | WO 2000002887  | A2   | 20000120 | WO 1999-US15450 | 19990709 <-- |
|      | WO 2000002887  | A3   | 20000629 |                 |              |
|      | W: CA, JP  |      |          |                 |              |
|      | RW: AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE |      |          |                 |              |
|      | US 6395916   | B1   | 20020528 | US 1998-113478  | 19980710 <-- |
|      | US 6307087   | B1   | 20011023 | US 1999-231315  | 19990113 <-- |
|      | CA 2336691   | AA   | 20000120 | CA 1999-2336691 | 19990709 <-- |
|      | EP 1097158   | A2   | 20010509 | EP 1999-933785  | 19990709 <-- |
|      | R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, FI  |      |          |                 |              |
| PRAI | JP 2002520328  | T2   | 20020709 | JP 2000-559117  | 19990709 <-- |
|      | US 1998-113478   | A    | 19980710 | <--             |              |
|      | US 1998-196855   | A    | 19981120 | <--             |              |
|      | US 1999-231315   | A    | 19990113 |                 |              |
|      | US 1999-239024   | A    | 19990127 |                 |              |
| OS   | WO 1999-US15450  | W    | 19990709 | <--             |              |
|      | MARPAT 132:108101  |      |          |                 |              |
| GI   |  |      |          |                 |              |



AB The present invention relates to the prepn. of novel biaryl phosphine and amine ligands (I) [wherein A and B = independently fused monocyclic or polycyclic cycloalkyl, cycloalkenyl, aryl, or heterocyclic rings of 4-8 atoms; X = NR<sub>2</sub>, PR<sub>2</sub>, AsR<sub>2</sub>, OR, or SR; Y = NR<sub>2</sub>, PR<sub>2</sub>, AsR<sub>2</sub>, OR, SR, SiR<sub>3</sub>, alkyl, or H; R-R<sub>6</sub> = independently H, halogen, (hetero)alkyl, alkenyl, alkynyl, hydroxy, alkoxy, silyloxy, amino, nitro, sulphydryl, amide, carbonyl, ketone, anhydride, silyl, thioalkyl, ketone, ester, nitrile,

(hetero)aryl, etc.] for transition metals and their use in metal-catalyzed carbon-heteroatom and carbon-carbon bond-forming reactions. Unexpected improvements over the prior art were demonstrated in transition metal-catalyzed aryl amination reactions, Suzuki couplings giving both biaryl and alkylaryl products, arylations and vinylations at the position .alpha. to carbonyl groups, and carbon-oxygen bond formation. The ligands and methods of the invention enable transformations utilizing aryl chlorides and bromides at room temp. at synthetically useful rates with extremely small amts. of catalyst relative to the limiting reagent. For example, coupling of p-chlorobenzonitrile and morpholine was catalyzed by 2.5 mol% Pd<sub>2</sub>(dba)<sub>3</sub>, 7.5 mol% of 2-(N,N-dimethylamino)-2'-  
(dicyclohexylphosphino)biphenyl, and NaOBu-t in DME at room temp. to provide 4-(4-morpholinyl)benzonitrile in 96% yield. Thus, the subject processes provide improvements in many features of the transition metal-catalyzed reactions, including the range of suitable substrates, reaction conditions, and efficiency.

ST biaryl phosphine ammine ligand prep transition metal catalyst; amination aryl chloride bromide palladium catalysts; Suzuki coupling aryl chloride bromide palladium catalysts; ketone arylation vinylation palladium catalysts; etherification palladium catalysts

IT Amines, preparation

RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation); USES (Uses)

(arom.; prepn. of biaryl phosphine and amine ligands for improved palladium-catalyzed amination reactions, Suzuki couplings, arylations, vinylations, and carbon-oxygen bond formation reactions)

IT Ethers, preparation

Ketones, preparation

RL: SPN (Synthetic preparation); PREP (Preparation)

(arom.; prepn. of biaryl phosphine and amine ligands for improved palladium-catalyzed amination reactions, Suzuki couplings, arylations, vinylations, and carbon-oxygen bond formation reactions)

IT Aryl halides

Aryl halides

RL: RCT (Reactant); RACT (Reactant or reagent)

(aryl chlorides; prepn. of biaryl phosphine and amine ligands for improved palladium-catalyzed amination reactions, Suzuki couplings, arylations, vinylations, and carbon-oxygen bond formation reactions)

IT Chlorides, reactions

Chlorides, reactions

RL: RCT (Reactant); RACT (Reactant or reagent)

(aryl; prepn. of biaryl phosphine and amine ligands for improved palladium-catalyzed amination reactions, Suzuki couplings, arylations, vinylations, and carbon-oxygen bond formation reactions)

IT Transition metal complexes

Transition metal complexes

RL: CAT (Catalyst use); USES (Uses)

(phosphine; prepn. of biaryl phosphine and amine ligands for improved palladium-catalyzed amination reactions, Suzuki couplings, arylations, vinylations, and carbon-oxygen bond formation reactions)

IT Amination

Amination catalysts

Arylation

Arylation catalysts

Cross-coupling reaction catalysts

Etherification

Etherification catalysts

Suzuki coupling reaction

Vinylation

Vinylation catalysts

(prepn. of biaryl phosphine and amine ligands for improved palladium-catalyzed amination reactions, Suzuki couplings, arylations, vinylations, and carbon-oxygen bond formation reactions)

IT Phosphines  
 RL: CAT (Catalyst use); USES (Uses)  
 (prepn. of biaryl phosphine and amine ligands for improved palladium-catalyzed amination reactions, Suzuki couplings, arylations, vinylations, and carbon-oxygen bond formation reactions)

IT Biaryls  
 RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation); USES (Uses)  
 (prepn. of biaryl phosphine and amine ligands for improved palladium-catalyzed amination reactions, Suzuki couplings, arylations, vinylations, and carbon-oxygen bond formation reactions)

IT Aryl bromides  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (prepn. of biaryl phosphine and amine ligands for improved palladium-catalyzed amination reactions, Suzuki couplings, arylations, vinylations, and carbon-oxygen bond formation reactions)

IT Phosphines  
 Phosphines  
 RL: CAT (Catalyst use); USES (Uses)  
 (transition metal complexes; prepn. of biaryl phosphine and amine ligands for improved palladium-catalyzed amination reactions, Suzuki couplings, arylations, vinylations, and carbon-oxygen bond formation reactions)

IT 534-17-8, Dicesium carbonate 3375-31-3, Diacetatopalladium 6476-37-5, Dicyclohexylphenylphosphine 14221-01-3, Tetrakis(triphenylphosphine)palladium 31570-04-4 51364-51-3, Tris(dibenzylideneacetone)dipalladium 54000-83-8, 2,6-Dimethoxyphenyl-di-t-butylphosphine 71042-54-1 74286-11-6 76189-56-5 91548-08-2 100165-88-6 133545-16-1 136779-28-7 139139-92-7 145964-33-6 149341-34-4 155806-35-2 213774-71-1 224311-49-3 247940-06-3 255837-14-0, 2,4,6-Trimethoxyphenyl-di-t-butylphosphine 255837-17-3 255837-19-5 255882-15-6 255882-16-7 255882-17-8 255882-18-9  
 RL: CAT (Catalyst use); USES (Uses)  
 (catalyst; prepn. of biaryl phosphine and amine ligands for improved palladium-catalyzed amination reactions, Suzuki couplings, arylations, vinylations, and carbon-oxygen bond formation reactions)

IT 698-00-0P 4688-76-0P 18937-92-3P 20837-12-1P, 2-Bromo-2'-methoxy-1,1'-biphenyl 59734-92-8P 75295-57-7P 89291-23-6P 89787-12-2P, 2-Isopropylphenylboronic acid 128796-39-4P, 4-(Trifluoromethyl)phenylboronic acid 224311-57-3P 224311-58-4P 224311-59-5P 251320-87-3P, 2-Bromo-2'-methylbiphenyl 251320-89-5P, 2-Bromo-2'-isopropylbiphenyl 255837-15-1P, 2-Bromo-4'-(trifluoromethyl)biphenyl 255837-16-2P 255837-18-4P  
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)  
 (intermediate; prepn. of biaryl phosphine and amine ligands for improved palladium-catalyzed amination reactions, Suzuki couplings, arylations, vinylations, and carbon-oxygen bond formation reactions)

IT 213697-53-1P  
 RL: CAT (Catalyst use); RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent); USES (Uses)  
 (prepd. catalyst; prepn. of biaryl phosphine and amine ligands for improved palladium-catalyzed amination reactions, Suzuki couplings, arylations, vinylations, and carbon-oxygen bond formation reactions)

IT 224311-51-7P, 2-(Di-tert-butylphosphino)biphenyl 224311-52-8P 224311-54-0P 224311-55-1P 251320-85-1P, 2-(Dicyclohexylphosphino)-2'-isopropylbiphenyl 251320-86-2P, 2-(Dicyclohexylphosphino)-2'-methylbiphenyl 255835-81-5P 255835-82-6P 255835-83-7P, 2-(Di-t-butylphosphino)-4'-(trifluoromethyl)biphenyl 255835-84-8P, 2-(Di-t-butylphosphino)-2'-(isopropyl)biphenyl 255835-85-9P 255836-32-9P 255836-65-8P 255836-67-0P 255836-68-1P, 1-[2-(Dicyclohexylphosphino)phenyl]naphthalene 255836-69-2P,

## 1-[2-(Di-t-butylphosphino)phenyl]naphthalene 255882-14-5P

RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation); USES (Uses)

(prepd. catalyst; prepn. of biaryl phosphine and amine ligands for improved palladium-catalyzed amination reactions, Suzuki couplings, arylations, vinylations, and carbon-oxygen bond formation reactions)

IT 62-53-3, Benzenamine, reactions 75-97-8 88-05-1 88-69-7 90-04-0  
 91-55-4 93-55-0, Propiophenone 95-65-8 95-68-1 95-72-7 96-22-0,  
 3-Pantanone 98-54-4 98-80-6 98-86-2, reactions 99-02-5 99-90-1  
 99-91-2 100-00-5, 1-Chloro-4-nitrobenzene 100-01-6, reactions  
 100-42-5, reactions 100-46-9, Benzenemethanamine, reactions 100-61-8,  
 reactions 103-69-5 103-88-8, 4'-Bromoacetanilide 104-92-7 104-94-9  
 105-53-3, Diethyl malonate 106-38-7 106-39-8 106-41-2, 4-Bromophenol  
 106-43-4 106-49-0, reactions 108-41-8 108-44-1, reactions  
 108-91-8, Cyclohexanamine, reactions 108-94-1, Cyclohexanone, reactions  
 109-01-3 109-04-6 109-09-1 110-89-4, Piperidine, reactions  
 110-91-8, Morpholine, reactions 111-26-2, 1-Hexanamine 111-92-2  
 119-61-9, Benzophenone, reactions 120-72-9, Indole, reactions 122-00-9  
 122-39-4, Diphenylamine, reactions 123-75-1, Pyrrolidine, reactions  
 141-97-9 280-64-8, 9-BBN 392-83-6, 2-Bromobenzotrifluoride 399-52-0  
 402-43-7, 4-(Trifluoromethyl)phenyl bromide 460-00-4,  
 1-Bromo-4-fluorobenzene 502-42-1, Cycloheptanone 504-02-9,  
 1,3-Cyclohexanedione 529-34-0 530-93-8, .beta.-Tetralone 540-88-5,  
 tert-Butyl acetate 553-94-6 556-96-7 557-93-7, 2-Bromopropene  
 563-80-4 565-69-5 565-80-0 576-22-7 576-26-1 583-53-9,  
 1,2-Dibromobenzene 583-55-1, 2-Bromoiodobenzene 586-77-6 588-72-7,  
 trans-.beta.-Bromostyrene 590-15-8, trans-1-Bromopropene 591-20-8  
 592-41-6, 1-Hexene, reactions 615-36-1, 2-Bromoaniline 618-45-1  
 618-89-3 619-42-1 623-00-7, 4-Bromobenzonitrile 623-03-0 623-12-1  
 624-31-7 626-55-1, 3-Bromopyridine 626-60-8, 3-Chloropyridine  
 645-36-3 765-30-0, Cyclopropylamine 766-51-8 766-84-7 778-82-5  
 782-17-2 872-31-1, 3-Bromo thiophene 873-32-5, 2-Chlorobenzonitrile  
 930-29-0, 1-Chlorocyclopentene 931-51-1, Cyclohexylmagnesium chloride  
 948-65-2 1003-09-4, 2-Bromo thiophene 1013-88-3, Benzophenone imine  
 1079-66-9, Chlorodiphenylphosphine 1122-91-4, 4-Bromobenzaldehyde  
 1122-95-8 1126-46-1 1450-65-3 1590-08-5 2038-03-1,  
 4-Morpholineethanamine 2052-07-5, 2-Bromobiphenyl 2142-68-9,  
 2'-Chloroacetophenone 2398-37-0 2635-13-4 2845-89-8 2856-63-5,  
 2-Chlorobenzyl cyanide 2905-65-9 3972-65-4, 1-Bromo-4-t-butylbenzene  
 4079-52-1 4541-32-6 5350-57-2 5619-07-8, DL-Phenylalanine methyl  
 ester hydrochloride 5720-06-9 5798-75-4, Ethyl 4-bromobenzoate  
 5892-99-9 6781-98-2 7051-16-3 7073-94-1, 2-Bromo isopropylbenzene  
 7524-50-7, L-Phenylalanine methyl ester hydrochloride 7598-28-9  
 13716-10-4, Chlorodi-tert-butylphosphine 13922-41-3, 1-Naphthylboronic  
 acid 15499-27-1 16081-16-6 16419-60-6 16523-54-9,  
 Chlorodicyclohexylphosphine 17496-14-9, 2-Methylindanone 17763-70-1  
 17763-80-3 17789-14-9, 2-(3-Bromophenyl)1,3-dioxolane 17933-03-8  
 18982-54-2, 2-Bromobenzyl alcohol 22237-13-4, 4-Ethoxyphenylboronic acid  
 22867-74-9 24544-04-5 27505-78-8 27752-24-5 36800-95-0,  
 4-Cyanophenyl tosylate 40138-16-7, 2-Formylphenylboronic acid  
 41085-43-2, 2-Bromo-3-nitrotoluene 41492-05-1 42371-64-2 53847-33-9  
 66107-29-7 66107-32-2 74866-28-7, 2,2'-Dibromo-1,1'-binaphthyl  
 100379-00-8 100717-47-3 109613-00-5 112042-84-9 154318-75-9  
 157282-19-4 158266-43-4 204841-19-0, 3-Acetylphenylboronic acid  
 207611-58-3 255837-20-8 255837-21-9 255837-22-0 255837-23-1

RL: RCT (Reactant); RACT (Reactant or reagent)

(starting material; prepn. of biaryl phosphine and amine ligands for improved palladium-catalyzed amination reactions, Suzuki couplings, arylations, vinylations, and carbon-oxygen bond formation reactions)

IT 78235-91-3P 213697-67-7P  
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)

(starting material; prepn. of biaryl phosphine and amine ligands for

improved palladium-catalyzed amination reactions, Suzuki couplings, arylations, vinylations, and carbon-oxygen bond formation reactions)

IT 251320-80-6P, N-(Diphenylmethylene)-2-bromoaniline  
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)

(synthetic product; prepn. of biaryl phosphine and amine ligands for improved palladium-catalyzed amination reactions, Suzuki couplings, arylations, vinylations, and carbon-oxygen bond formation reactions)

IT 86-26-0P 92-69-3P, 4-Hydroxybiphenyl 92-91-1P, 4-Acetyl biphenyl 92-93-3P, 4-Nitro biphenyl 101-70-2P, 4,4'-Dimethoxydiphenylamine 121-00-6P 613-37-6P, 4-Methoxybiphenyl 620-83-7P 620-93-9P, Di-p-tolylamine 644-08-6P, 4-Methylbiphenyl 720-75-2P, Methyl 4-phenylbenzoate 730-11-0P, 4-Methoxy-4'-nitrodiphenylamine 774-52-7P, N-(4-Methylphenyl)piperidine 825-54-7P 825-55-8P, 2-Phenylthiophene 1208-86-2P 1625-92-9P, 4-t-Butylbiphenyl 2142-66-7P, 2-Acetyl biphenyl 2920-38-9P, 4-Cyanobiphenyl 2928-43-0P, 2-(Hydroxymethyl)biphenyl 3077-16-5P, N-(4-Methylphenyl)morpholine 3470-65-3P 3976-34-9P, 2,6-Dimethylbiphenyl 4036-43-5P 4075-79-0P, N-Acetyl-4-aminobiphenyl 4316-51-2P, N-(4-Methoxyphenyl)-N,N-diphenylamine 4316-53-4P 4496-49-5P 4787-76-2P, N-(2-Methoxyphenyl)pyrrolidine 5031-78-7P 5405-15-2P, N-Benzyl-p-toluidine 5405-19-6P 6574-15-8P, N-(4-Nitrophenyl)piperidine 6935-27-9P, N-Benzyl-2-aminopyridine 7372-85-2P, 2,5-Dimethylbiphenyl 10273-87-7P 10282-31-2P, N-(4-Cyanophenyl)morpholine 15359-99-6P 15360-00-6P 16251-99-3P 16819-50-4P, N-(2,6-Dimethylphenyl)benzylamine 17057-88-4P, 3,5-Dimethylbiphenyl 17952-07-7P 19853-10-2P, [1,1'-Biphenyl]-2-acetonitrile 21218-94-0P 23600-89-7P 23676-05-3P 23699-65-2P, N-(3-Acetylphenyl)aniline 23951-29-3P 24255-25-2P, N-(2-Pyridyl)morpholine 25539-14-4P 25699-92-7P, N-(4-Cyanophenyl)indole 25700-23-6P, N-(3-Pyridyl)indole 27347-14-4P 31144-33-9P 31603-95-9P, 4-tert-Butyl-1-tert-butyloxybenzene 34160-16-2P 35393-20-5P, N-(Diphenylmethylene)-4-nitroaniline 38158-65-5P 38869-05-5P 39253-43-5P 39910-98-0P, N-(4-Acetylphenyl)morpholine 50798-94-2P, N-(2-Methoxyphenyl)benzylamine 50910-08-2P, N-(2-Pyridyl)-N,N-diphenylamine 51580-77-9P 51786-49-3P 52351-44-7P, N-(4-Methoxyphenyl)-2-phenylindole 54480-44-3P, 4-Methoxy-4'-(dimethylamino)diphenylamine 54660-04-7P, N-(4-Methoxyphenyl)pyrrolidine 55251-46-2P 56052-33-6P 56506-60-6P, N-(4-Methylphenyl)hexylamine 56915-80-1P, 1-(3-Acetylphenyl)-4-methylpiperazine 60893-66-5P 61394-81-8P 62787-14-8P 62787-15-9P 62790-83-4P 62790-85-6P 68856-26-8P 70945-85-6P 75201-55-7P 75934-30-4P 76650-29-8P, 4-Acetyl-3'-methylbiphenyl 76708-72-0P 76708-78-6P, 2,5,3'-Trimethylbiphenyl 77422-28-7P 81693-80-3P, 4-Hexylanisole 82749-62-0P 83188-35-6P 84736-47-0P, N-(4-t-Butylphenyl)morpholine 84736-54-9P, 2-(4-Methoxyphenyl)-3-pentanone 84839-92-9P 84839-93-0P 91949-95-0P, 4-Isopropoxybenzonitrile 92495-53-9P, 4-Methyl-2'-methoxybiphenyl 92670-29-6P, N-(3-Pyridyl)morpholine 93597-01-4P, N-(4-Methoxyphenyl)indole 94540-42-8P 94959-58-7P 97053-04-8P 97413-60-0P 114081-08-2P 114772-53-1P 116267-90-4P, N-(3-Thiophenyl)-N,N-diphenylamine 123324-87-8P 124043-95-4P 129644-26-4P 137445-01-3P 138900-16-0P, N-(4-Fluorophenyl)indole 138900-19-3P 146803-96-5P 167283-32-1P, N-(4-Methylphenyl)indole 171092-38-9P, 3-(3-Acetylphenyl)pyridine 172878-95-4P 174307-96-1P 175696-73-8P, N-(3-Cyanophenyl)pyrrolidine 179487-70-8P 180336-54-3P, N-(2,5-Dimethylphenyl)-N-methylaniline 183135-51-5P, N-Methyl-N-(3-pyridyl)aniline 183135-52-6P 185259-34-1P, N-(4-t-Butylphenyl)piperidine 188026-55-3P, N,N-Dibutyl-4-t-butylaniline 188026-64-4P, N-Ethyl-N-(3,5-dimethylphenyl)aniline 188026-74-6P 196604-19-0P 196604-21-4P 196604-24-7P 197172-67-1P 197172-69-3P 197640-99-6P 202802-70-8P 211292-60-3P 211292-66-9P, 2,6-Diisopropyl-2',6'-dimethyldiphenylamine 212382-74-6P 213014-13-2P 213697-51-9P 213697-52-0P, 2,6-Dimethyl-N-hexylaniline 213697-65-5P,

1,1-Bis(4-methylphenyl)-3-methyl-2-butanone 213697-66-6P 215394-88-0P  
 223248-27-9P 223655-23-0P 224311-62-0P 224311-63-1P 224311-65-3P  
 224311-66-4P 224311-67-5P 224311-68-6P 224311-69-7P 224311-70-0P  
 224311-72-2P 224311-73-3P 224311-74-4P 224311-75-5P 224311-76-6P  
 226569-78-4P 226917-75-5P, N-(4-Cyanophenyl)hexylamine 247940-07-4P,  
 N-Methyl-N-(3,5-dimethoxyphenyl)aniline 247940-08-5P 251320-76-0P  
 251320-77-1P, 4-Formyl-4'-ethoxybiphenyl 251320-78-2P 251320-79-3P  
 251320-81-7P, 3-Acetyl-3',5'-dimethoxybiphenyl 251320-82-8P  
 251320-83-9P 251320-84-0P, 2-Methoxy-2'-acetyl biphenyl 253768-96-6P,  
 N-(3-Cyanophenyl)benzylamine 255835-86-0P 255835-87-1P 255835-88-2P  
 255835-89-3P 255835-90-6P 255835-91-7P, N-(2,6-  
 Dimethylphenyl)morpholine 255835-92-8P 255835-93-9P,  
 N-(4-t-Butylphenyl)benzylamine 255835-94-0P, N-(3,4-  
 Dimethylphenyl)pyrrolidine 255835-95-1P, 2-Methoxy-4'-cyanodiphenylamine  
 255835-96-2P 255835-97-3P 255835-98-4P 255835-99-5P 255836-00-1P  
 255836-01-2P 255836-02-3P 255836-04-5P, N-(2-Methoxyphenyl)-N-(3-  
 methoxyphenyl)-N-(4-methoxyphenyl)amine 255836-06-7P,  
 N-(4-Dimethylaminophenyl)-N-(4-methoxyphenyl)-N-(3-methylphenyl)amine  
 255836-08-9P, N-(2,4-Dimethylphenyl)-N-(4-methoxyphenyl)-N-(3-  
 methylphenyl)amine 255836-10-3P 255836-12-5P 255836-14-7P,  
 N-(4-Butylphenyl)-N-(4-methoxyphenyl)-N-(4-methylphenyl)amine  
 255836-15-8P, N-(2,5-Dimethylphenyl)-N-(3,5-dimethylphenyl)-N-(4-  
 methylphenyl)amine 255836-17-0P 255836-19-2P, N-(4-tert-  
 Butylphenyl)indole 255836-21-6P 255836-23-8P, N-Cyclopropyl-4-tert-  
 butylaniline 255836-25-0P, N-Cyclopropyl-2,5-dimethylaniline  
 255836-28-3P 255836-30-7P 255836-36-3P 255836-38-5P 255836-39-6P  
 255836-41-0P 255836-43-2P 255836-44-3P 255836-45-4P,  
 2-Methyl-4-(4-butylphenyl)-3-pentanone 255836-46-5P 255836-48-7P  
 255836-50-1P 255836-52-3P 255836-54-5P, 2-(3-Hydroxyphenyl)-3-  
 pentanone 255836-56-7P, 2,4-Dimethyl-2-(4-t-butylphenyl)-3-pentanone  
 255836-57-8P 255836-59-0P 255836-61-4P 255836-63-6P 255836-70-5P,  
 N-(4-t-Butylphenyl)-2-phenylindole 255836-72-7P 255836-74-9P,  
 N-(3,5-Dimethylphenyl)-2,3-dimethylindole 255836-76-1P,  
 N-(4-t-Butylphenyl)-2,3,7-trimethylindole 255836-78-3P 255836-80-7P,  
 N-(2-Pyridyl)-7-ethylindole 255836-82-9P, N-(3,5-Dimethylphenyl)-7-  
 ethylindole 255836-84-1P 255836-86-3P 255836-88-5P 255836-90-9P  
 255836-92-1P 255836-94-3P 255836-95-4P 255836-96-5P 255836-97-6P  
 255836-98-7P 255836-99-8P 255837-00-4P 255837-01-5P 255837-02-6P  
 255837-03-7P

RL: SPN (Synthetic preparation); PREP (Preparation)

(synthetic product; prepn. of biaryl phosphine and amine ligands for improved palladium-catalyzed amination reactions, Suzuki couplings, arylations, vinylations, and carbon-oxygen bond formation reactions)

IT 255837-04-8P 255837-05-9P 255837-06-0P 255837-07-1P 255837-08-2P  
 255837-09-3P 255837-10-6P 255837-11-7P 255837-12-8P 255837-13-9P

RL: SPN (Synthetic preparation); PREP (Preparation)

(synthetic product; prepn. of biaryl phosphine and amine ligands for improved palladium-catalyzed amination reactions, Suzuki couplings, arylations, vinylations, and carbon-oxygen bond formation reactions)

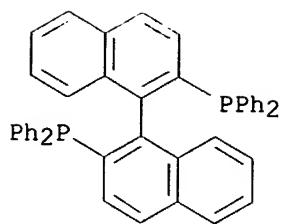
IT 76189-56-5 100165-88-6 139139-92-7  
 145964-33-6 213774-71-1

RL: CAT (Catalyst use); USES (Uses)

(catalyst; prepn. of biaryl phosphine and amine ligands for improved palladium-catalyzed amination reactions, Suzuki couplings, arylations, vinylations, and carbon-oxygen bond formation reactions)

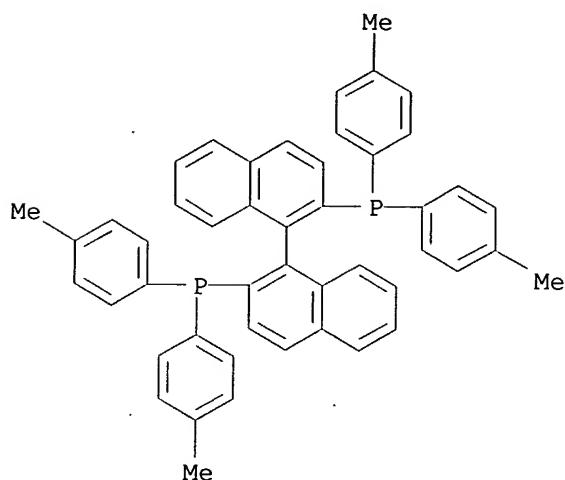
RN 76189-56-5 HCAPLUS

CN Phosphine, (1S)-[1,1'-binaphthalene]-2,2'-diylbis[diphenyl- (9CI) (CA INDEX NAME)]



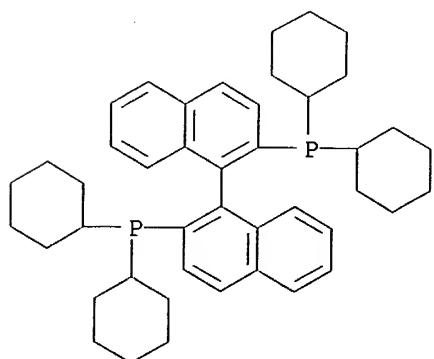
RN 100165-88-6 HCAPLUS

CN Phosphine, (1S)-[1,1'-binaphthalene]-2,2'-diylbis[bis(4-methylphenyl)]- (9CI) (CA INDEX NAME)



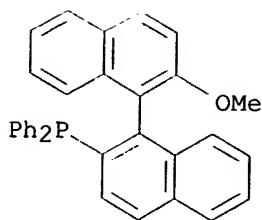
RN 139139-92-7 HCAPLUS

CN Phosphine, (1R)-[1,1'-binaphthalene]-2,2'-diylbis[dicyclohexyl- (9CI) (CA INDEX NAME)

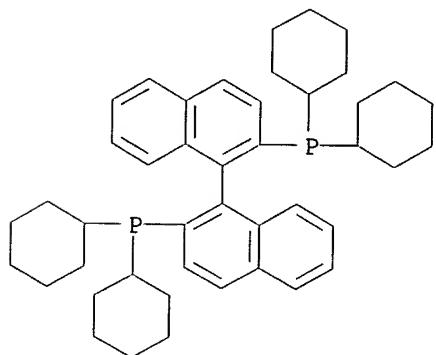


RN 145964-33-6 HCAPLUS

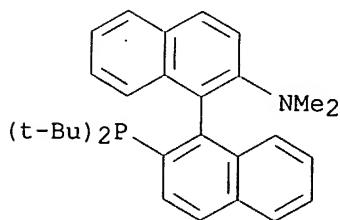
CN Phosphine, [(1R)-2'-methoxy[1,1'-binaphthalen]-2-yl]diphenyl- (9CI) (CA INDEX NAME)



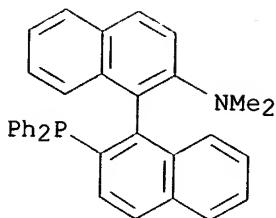
RN 213774-71-1 HCPLUS  
 CN Phosphine, [1,1'-binaphthalene]-2,2'-diylbis[dicyclohexyl- (9CI) (CA INDEX NAME)



IT 224311-52-8P 255882-14-5P  
 RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation); USES (Uses)  
 (prepd. catalyst; prepn. of biaryl phosphine and amine ligands for improved palladium-catalyzed amination reactions, Suzuki couplings, arylations, vinylations, and carbon-oxygen bond formation reactions)  
 RN 224311-52-8 HCPLUS  
 CN [1,1'-Binaphthalen]-2-amine, 2'-(bis(1,1-dimethylethyl)phosphino)-N,N-dimethyl- (9CI) (CA INDEX NAME)



RN 255882-14-5 HCPLUS  
 CN [1,1'-Binaphthalen]-2-amine, 2'-(diphenylphosphino)-N,N-dimethyl- (9CI) (CA INDEX NAME)



L34 ANSWER 4 OF 19 HCAPLUS COPYRIGHT 2003 ACS  
 AN 1999:566015 HCAPLUS  
 DN 131:199501  
 TI Transition metal-catalyzed arylation of hydrazines, hydrazone, hydroxylamines, and oximes using activated aromatic compounds.  
 IN Buchwald, Stephen L.; Wagaw, Seble; Geis, Oliver  
 PA Massachusetts Institute of Technology, USA  
 SO PCT Int. Appl., 97 pp.  
 CODEN: PIXXD2  
 DT Patent  
 LA English  
 IC ICM C07C243-00  
 CC 25-5 (Benzene, Its Derivatives, and Condensed Benzenoid Compounds)  
 Section cross-reference(s): 27

FAN.CNT '1

|      | PATENT NO.  | KIND | DATE         | APPLICATION NO. | DATE         |
|------|---|------|--------------|-----------------|--------------|
| PI   | WO 9943643  | A2   | 19990902     | WO 1999-US4217  | 19990226 <-- |
|      | WO 9943643  | A3   | 19991021     |                 |              |
|      | W: CA, JP   |      |              |                 |              |
|      | RW: AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, |      |              |                 |              |
|      | PT, SE  |      |              |                 |              |
|      | US 6235936  | B1   | 20010522     | US 1998-30936   | 19980226 <-- |
|      | CA 2322194  | AA   | 19990902     | CA 1999-2322194 | 19990226 <-- |
|      | EP 1058678  | A2   | 20001213     | EP 1999-908515  | 19990226 <-- |
|      | EP 1058678  | B1   | 20021211     |                 |              |
|      | R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT,  |      |              |                 |              |
|      | IE, FI  |      |              |                 |              |
|      | JP 2002504535   | T2   | 20020212     | JP 2000-533402  | 19990226 <-- |
|      | AT 229499   | E    | 20021215     | AT 1999-908515  | 19990226 <-- |
|      | US 2001031894   | A1   | 20011018     | US 2001-765072  | 20010118 <-- |
|      | US 6465693  | B2   | 20021015     |                 |              |
| PRAI | US 1998-30936   | A    | 19980226 <-- |                 |              |
|      | US 1998-55557   | A    | 19980406 <-- |                 |              |
|      | WO 1999-US4217  | W    | 19990226     |                 |              |

OS CASREACT 131:199501

AB Hydrazines, hydrazone, hydroxylamines, and oximes were arylated using activated arom. compds. and transition metal catalysts. Thus, PhNHNH<sub>2</sub>, 4-BrC<sub>6</sub>H<sub>4</sub>Me, Pd(OAc)<sub>2</sub>, BINAP, NaOCMe<sub>3</sub>, and (Me<sub>2</sub>CH)<sub>2</sub>NH were heated together at 80.degree. for 1 h; (CF<sub>3</sub>CO)<sub>2</sub>O and Et<sub>3</sub>N were added to the residue in CH<sub>2</sub>C<sub>2</sub> to give 70% N-phenyl-N-4-tolyl-N'-trifluoroacetic hydrazide.

ST arylation hydrazine hydrazone hydroxylamine oxime transition metal catalyst; vinylation hydrazine hydrazone hydroxylamine oxime transition metal catalyst

IT Arylation catalysts  
Vinylation catalysts

(transition metal compds., phosphines, bases; transition metal-catalyzed arylation of hydrazines, hydrazone, hydroxylamines, and oximes using activated arom. compds.)

IT Arylation  
Vinylation

(transition metal-catalyzed arylation of hydrazines, hydrazones, hydroxylamines, and oximes using activated arom. compds.)

IT Transition metal compounds  
 RL: CAT (Catalyst use); USES (Uses)  
 (transition metal-catalyzed arylation of hydrazines, hydrazones, hydroxylamines, and oximes using activated arom. compds.)

IT Hydrazones  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (transition metal-catalyzed arylation of hydrazines, hydrazones, hydroxylamines, and oximes using activated arom. compds.)

IT Oximes  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (transition metal-catalyzed arylation of hydrazines, hydrazones, hydroxylamines, and oximes using activated arom. compds.)

IT 3375-31-3, Palladium diacetate 7439-88-5D, Iridium, compds., uses 7439-89-6D, Iron, compds., uses 7440-02-0D, Nickel, compds., uses 7440-05-3D, Palladium, compds., uses 7440-06-4D, Platinum, compds., uses 7440-16-6D, Rhodium, compds., uses 7440-18-8D, Ruthenium, compds., uses 7440-48-4D, Cobalt, compds., uses 7440-50-8D, Copper, compds., uses 76189-56-5 161265-03-8 166330-10-5  
 RL: CAT (Catalyst use); USES (Uses)  
 (transition metal-catalyzed arylation of hydrazines, hydrazones, hydroxylamines, and oximes using activated arom. compds.)

IT 40113-76-6P 40594-87-4P 210536-89-3P 210536-91-7P 240482-58-0P  
 240482-64-8P 240482-68-2P 240482-69-3P  
 RL: IMF (Industrial manufacture); RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)  
 (transition metal-catalyzed arylation of hydrazines, hydrazones, hydroxylamines, and oximes using activated arom. compds.)

IT 606-88-2P 30769-69-8P 58263-75-5P 226065-35-6P 240482-52-4P  
 240482-53-5P 240482-54-6P 240482-55-7P 240482-56-8P 240482-57-9P  
 240482-67-1P 240482-70-6P 240482-71-7P  
 RL: IMF (Industrial manufacture); SPN (Synthetic preparation); PREP (Preparation)  
 (transition metal-catalyzed arylation of hydrazines, hydrazones, hydroxylamines, and oximes using activated arom. compds.)

IT 57-14-7, N,N-Dimethylhydrazine 78-93-3, 2-Butanone, reactions 90-11-9, 1-Bromonaphthalene 90-90-4, 4-Bromobenzophenone 92-66-0, 4-Bromobiphenyl 96-22-0, 3-Pentanone 100-39-0, Benzyl bromide 100-46-9, Benzylamine, reactions 100-63-0, Phenylhydrazine 104-92-7, 4-Bromoanisole 106-38-7, 4-Bromotoluene 106-39-8, 4-Chlorobromobenzene 106-49-0, p-Toluidine, reactions 108-86-1, Bromobenzene, reactions 108-94-1, Cyclohexanone, reactions 111-71-7, Heptanal 122-66-7, 1,2-Diphenylhydrazine 123-76-2, Levulinic acid 302-01-2D, Hydrazine, compds., reactions 402-43-7, 4-Bromobenzotrifluoride 407-25-0, Trifluoroacetic anhydride 530-47-2, 1,1-Diphenylhydrazine hydrochloride 556-96-7, 5-Bromo-m-xylene 578-57-4, 2-Bromoanisole 591-78-6, 2-Hexanone 626-55-1, 3-Bromopyridine 694-80-4, 2-Chlorobromobenzene 823-85-8, 4-Fluorophenylhydrazine hydrochloride 870-46-2, tert-Butyl carbamate 2859-78-1, 4-Bromoveratrole 5350-57-2, Benzophenone hydrazone 6156-08-7, Cyclohexanone hydrazone 6952-59-6, 3-Bromobenzonitrile 7699-31-2, 1,2-Diethylhydrazine dihydrochloride 7803-49-8D, Hydroxylamine, compds., reactions 98327-87-8, Binap 240482-76-2  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (transition metal-catalyzed arylation of hydrazines, hydrazones, hydroxylamines, and oximes using activated arom. compds.)

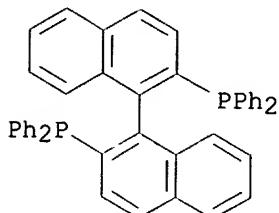
IT 36684-65-8P 55542-85-3P 102173-26-2P 107455-62-9P 110178-49-9P  
 124043-95-4P 240482-60-4P 240482-63-7P 240482-65-9P 240482-72-8P  
 240482-73-9P 240482-74-0P 240482-75-1P  
 RL: SPN (Synthetic preparation); PREP (Preparation)  
 (transition metal-catalyzed arylation of hydrazines, hydrazones, hydroxylamines, and oximes using activated arom. compds.)

IT 76189-56-5

RL: CAT (Catalyst use); USES (Uses)  
 (transition metal-catalyzed arylation of hydrazines, hydrazone,  
 hydroxylamines, and oximes using activated arom. compds.)

RN 76189-56-5 HCPLUS

CN Phosphine, (1S)-[1,1'-binaphthalene]-2,2'-diylbis[diphenyl- (9CI) (CA INDEX NAME)

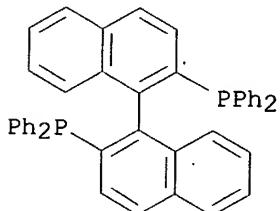


IT 98327-87-8, Binap

RL: RCT (Reactant); RACT (Reactant or reagent)  
 (transition metal-catalyzed arylation of hydrazines, hydrazone,  
 hydroxylamines, and oximes using activated arom. compds.)

RN 98327-87-8 HCPLUS

CN Phosphine, [1,1'-binaphthalene]-2,2'-diylbis[diphenyl- (9CI) (CA INDEX NAME)



L34 ANSWER 5 OF 19 HCPLUS COPYRIGHT 2003 ACS

AN 1998:577201 HCPLUS

DN 129:275663

TI A Highly Active Catalyst for Palladium-Catalyzed Cross-Coupling Reactions:  
 Room-Temperature Suzuki Couplings and Amination of Unactivated Aryl  
 ChloridesAU Old, David W.; Wolfe, John P.; Buchwald, Stephen  
 L.CS Department of Chemistry, Massachusetts Institute of Technology, Cambridge,  
 MA, 02139, USASO Journal of the American Chemical Society (1998), 120(37),  
 9722-9723

CODEN: JACSAT; ISSN: 0002-7863

PB American Chemical Society

DT Journal

LA English

CC 25-1 (Benzene, Its Derivatives, and Condensed Benzenoid Compounds)

OS CASREACT 129:275663

AB Pd2(dba)3 and ligand 2-(dicyclohexylphosphino)-2'-(dimethylamino)biphenyl  
 catalyzed the amination of aryl chloride or bromides at room temp. Also,  
 Pd2(dba)3 or Pd(OAc)2 and ligand 2-(dicyclohexylphosphino)-2'-(dimethylamino)biphenyl  
 catalyzed the Suzuki coupling of aryl chloride or bromides with boron reagents at room temp.

ST palladium catalyst cross coupling reaction; amination aryl chloride

IT bromide palladium catalyst; Suzuki coupling aryl chloride bromide  
 3375-31-3, Palladium diacetate 51364-51-3, Pd2(DBA)3 213774-71-1  
 RL: CAT (Catalyst use); USES (Uses)  
 (palladium-catalyzed Suzuki coupling reactions or amination of aryl  
 chlorides or aryl bromides)

IT 213697-53-1P  
 RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation);  
 USES (Uses)  
 (palladium-catalyzed Suzuki coupling reactions or amination of aryl  
 chlorides or aryl bromides)

IT 95-72-7 98-80-6 99-90-1 99-91-2 100-46-9, Benzylamine, reactions  
 100-61-8, reactions 106-38-7 106-43-4 106-49-0, p-Toluidine,  
 reactions 110-91-8, Morpholine, reactions 111-26-2, Hexylamine  
 111-92-2, Dibutylamine 553-94-6 556-96-7 563-80-4 565-69-5  
 576-22-7 583-55-1, 2-Bromoiodobenzene 619-42-1 623-03-0 623-12-1  
 698-00-0 1126-46-1 5720-06-9 16523-54-9, Chlorodicyclohexylphosphine  
 17933-03-8 42371-64-2  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (palladium-catalyzed Suzuki coupling reactions or amination of aryl  
 chlorides or aryl bromides)

IT 89291-23-6P 213697-67-7P  
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT  
 (Reactant or reagent)  
 (palladium-catalyzed Suzuki coupling reactions or amination of aryl  
 chlorides or aryl bromides)

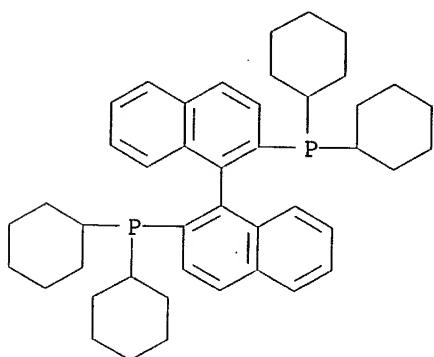
IT 613-37-6P, 4-Methoxybiphenyl 644-08-6P, 4-Methylbiphenyl 720-75-2P,  
 Methyl 4-biphenylcarboxylate 5405-15-2P 10282-31-2P 17057-88-4P,  
 3,5-Dimethylbiphenyl 23676-05-3P 27347-14-4P 31144-33-9P  
 38158-65-5P 39253-43-5P 39910-98-0P 55251-46-2P 76650-29-8P  
 76708-78-6P 81693-80-3P 82749-62-0P 92495-53-9P 174307-96-1P  
 180336-54-3P 197172-67-1P 213697-51-9P 213697-52-0P 213697-65-5P  
 213697-66-6P  
 RL: SPN (Synthetic preparation); PREP (Preparation)  
 (palladium-catalyzed Suzuki coupling reactions or amination of aryl  
 chlorides or aryl bromides)

RE.CNT 30 THERE ARE 30 CITED REFERENCES AVAILABLE FOR THIS RECORD

RE

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- (26) Wolfe, J; J Am Chem Soc 1997, V119, P6054 HCPLUS

(27) Wolfe, J; J Org Chem 1997, V62, P6066 HCAPLUS  
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 (29) Yamamoto, T; Tetrahedron Lett 1998, V39, P2367 HCAPLUS  
 (30) Zhang, X; J Chem Soc, Perkin Trans 1 1994, P2309 HCAPLUS  
 IT 213774-71-1  
 RL: CAT (Catalyst use); USES (Uses)  
 (palladium-catalyzed Suzuki coupling reactions or amination of aryl  
 chlorides or aryl bromides)  
 RN 213774-71-1 HCAPLUS  
 CN Phosphine, [1,1'-binaphthalene]-2,2'-diylbis[dicyclohexyl- (9CI) (CA  
 INDEX NAME)



L34 ANSWER 6 OF 19 HCAPLUS COPYRIGHT 2003 ACS  
 AN 1998:431153 HCAPLUS  
 DN 129:136056  
 TI A Palladium-Catalyzed Strategy for the Preparation of Indoles: A Novel  
 Entry into the Fischer Indole Synthesis  
 AU Wagaw, Seble; Yang, Bryant H.; Buchwald, Stephen L.  
 CS Department of Chemistry, Massachusetts Institute of Technology, Cambridge,  
 MA, 02139, USA  
 SO Journal of the American Chemical Society (1998), 120(26),  
 6621-6622  
 CODEN: JACSAT; ISSN: 0002-7863  
 PB American Chemical Society  
 DT Journal  
 LA English  
 CC 27-11 (Heterocyclic Compounds (One Hetero Atom))  
 AB A Fischer indole synthesis was accomplished by Pd-catalyzed cross coupling  
 of benzophenone hydrazone with aryl bromides to furnish N-arylhydrazones,  
 followed by hydrolysis in presence of a ketone. Purifn. of the  
 intermediate hydrazone was not necessary. The catalyst system included  
 Pd(OAc)<sub>2</sub> and either (S)- or (+-)-BINAP.  
 ST Fischer indole synthesis palladium catalyst; cross coupling benzophenone  
 hydrazone aryl bromide  
 IT Fischer indole synthesis  
 (palladium-catalyzed Fischer indole synthesis)  
 IT Cross-coupling reaction  
 Cross-coupling reaction catalysts  
 (palladium-catalyzed cross coupling of benzophenone hydrazone with aryl  
 bromides)  
 IT Aryl bromides  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (palladium-catalyzed cross coupling of benzophenone hydrazone with aryl  
 bromides)  
 IT Hydrazones  
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT

(Reactant or reagent)

(prepn. of N-arylhydrazones by palladium-catalyzed cross coupling of benzophenone hydrazone with aryl bromides)

IT 3375-31-3, Palladium diacetate 76189-56-5, (S)-BINAP  
98327-87-8, BINAP

RL: CAT (Catalyst use); USES (Uses)

(palladium-catalyzed Fischer indole synthesis)

IT 90-11-9, 1-Bromonaphthalene 92-66-0, 4-Bromobiphenyl 96-22-0, Diethyl ketone 98-86-2, Acetophenone, reactions 106-38-7, p-Bromotoluene 106-39-8, p-Bromochlorobenzene 108-94-1, Cyclohexanone, reactions 111-13-7, 2-Octanone 123-76-2 402-43-7, 4-Bromo(trifluoromethyl)benzene 556-96-7, 5-Bromo-m-xylene 563-80-4, Isopropyl methyl ketone 591-78-6, 2-Hexanone 2398-37-0, 3-Bromoanisole 2859-78-1, 4-Bromoveratrole 5350-57-2, Benzophenone hydrazone 6156-08-7, Cyclohexanone hydrazone 72530-28-0, 2-Octanone hydrazone

RL: RCT (Reactant); RACT (Reactant or reagent)

(palladium-catalyzed Fischer indole synthesis)

IT 40113-76-6P 40594-87-4P 40594-88-5P 210536-89-3P 210536-90-6P  
210536-91-7P 210536-92-8P

RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)

(palladium-catalyzed Fischer indole synthesis)

IT 33555-17-8P 34601-58-6P 36684-65-8P 55542-85-3P 110178-49-9P  
119266-78-3P 210536-93-9P 210536-94-0P 210536-95-1P 210536-96-2P

RL: SPN (Synthetic preparation); PREP (Preparation)

(palladium-catalyzed Fischer indole synthesis)

IT 865-48-5, tert-Butanol sodium salt

RL: NUU (Other use, unclassified); USES (Uses)

(prepn. of)

RE.CNT .15 THERE ARE 15 CITED REFERENCES AVAILABLE FOR THIS RECORD

RE

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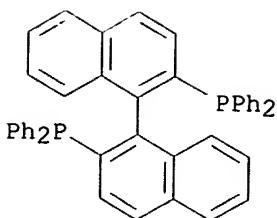
IT 76189-56-5, (S)-BINAP 98327-87-8, BINAP

RL: CAT (Catalyst use); USES (Uses)

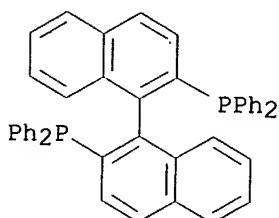
(palladium-catalyzed Fischer indole synthesis)

RN 76189-56-5 HCPLUS

CN Phosphine, (1S)-[1,1'-binaphthalene]-2,2'-diylbis[diphenyl- (9CI) (CA INDEX NAME)]

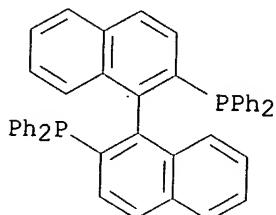


RN 98327-87-8 HCAPLUS  
 CN Phosphine, [1,1'-binaphthalene]-2,2'-diylbis[diphenyl- (9CI) (CA INDEX NAME)]

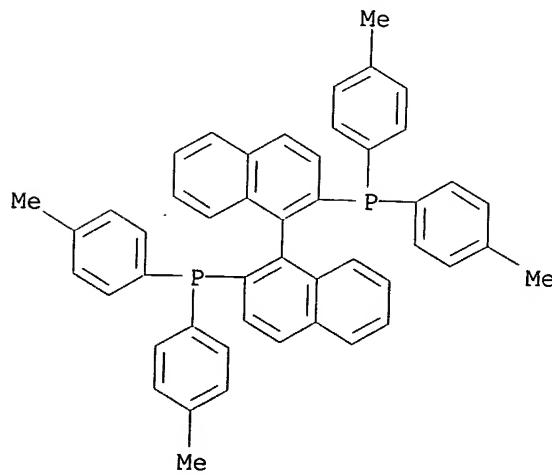


L34 ANSWER 7 OF 19 HCAPLUS COPYRIGHT 2003 ACS  
 AN 1997:720450 HCAPLUS  
 DN 127:331243  
 TI Palladium-Catalyzed .alpha.-Arylation of Ketones  
 AU Palucki, Michael; Buchwald, Stephen L.  
 CS Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA, 02139, USA  
 SO Journal of the American Chemical Society (1997), 119(45), 11108-11109  
 CODEN: JACSAT; ISSN: 0002-7863  
 PB American Chemical Society  
 DT Journal  
 LA English  
 CC 25-16 (Benzene, Its Derivatives, and Condensed Benzenoid Compounds)  
 Section cross-reference(s): 29  
 OS CASREACT 127:331243  
 AB The combination of Pd2(dba)3 and Tol-BINAP or BINAP in the presence of NaOBu-t catalyzes the reaction of aryl bromides with ketones to give .alpha.-aryl ketones in moderate to high yields. The regioselectivity of arylation of ketones contg. .alpha.,.alpha.'-hydrogens is high: Me > methylene .mchgt. methine. The degree of regioselectivity was found to be independent of the acidity of the .alpha.-hydrogen.  
 ST palladium catalyzed arylation ketone  
 IT Regiochemistry  
     (of palladium-catalyzed arylation of ketones by aryl bromides)  
 IT Arylation  
 IT Arylation catalysts  
     (palladium-catalyzed .alpha.-arylation of ketones by aryl bromides)  
 IT Aryl bromides  
 IT Ketones, reactions  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
     (palladium-catalyzed .alpha.-arylation of ketones by aryl bromides)  
 IT 51364-51-3, Tris(dibenzylideneacetone)dipalladium 98327-87-8,  
 BINAP 99646-28-3 100165-88-6  
 RL: CAT (Catalyst use); USES (Uses)  
     (palladium-catalyzed .alpha.-arylation of ketones by aryl bromides)

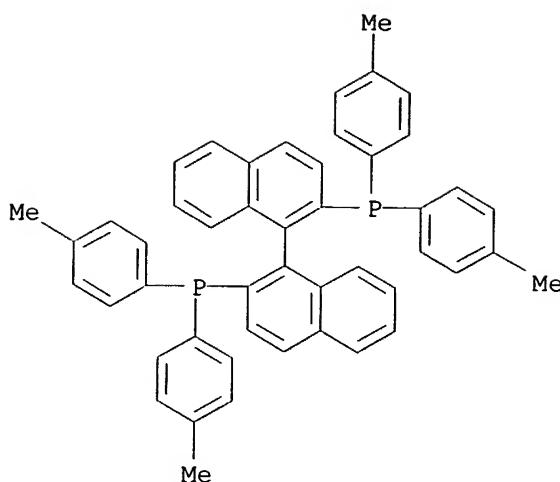
IT 75-97-8, tert-Butyl methyl ketone 92-66-0 93-55-0, Propiophenone  
 99-91-2 100-06-1 106-39-8 108-94-1, Cyclohexanone, reactions  
 553-94-6 556-96-7 563-80-4, Isopropyl methyl ketone 565-69-5, Ethyl  
 Isopropyl ketone 590-50-1 591-78-6, Butyl methyl ketone 623-00-7,  
 p-Bromobenzonitrile 781-35-1 1271-55-2, Acetylferrocene 2398-37-0  
 3162-29-6 3972-65-4 5892-99-9 17789-14-9 53847-33-9  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (palladium-catalyzed .alpha.-arylation of ketones by aryl bromides)  
 IT 119046-91-2P 197640-96-3P 197640-97-4P 197640-98-5P 197640-99-6P  
 197641-00-2P 197641-01-3P 197641-02-4P 197641-04-6P 197641-05-7P  
 RL: SPN (Synthetic preparation); PREP (Preparation)  
 (palladium-catalyzed .alpha.-arylation of ketones by aryl bromides)  
 IT 98327-87-8, BINAP 99646-28-3 100165-88-6  
 RL: CAT (Catalyst use); USES (Uses)  
 (palladium-catalyzed .alpha.-arylation of ketones by aryl bromides)  
 RN 98327-87-8 HCPLUS  
 CN Phosphine, [1,1'-binaphthalene]-2,2'-diylbis[diphenyl- (9CI) (CA INDEX NAME)



RN 99646-28-3 HCPLUS  
 CN Phosphine, (1R)-[1,1'-binaphthalene]-2,2'-diylbis[bis(4-methylphenyl)-  
 (9CI) (CA INDEX NAME)]



RN 100165-88-6 HCPLUS  
 CN Phosphine, (1S)-[1,1'-binaphthalene]-2,2'-diylbis[bis(4-methylphenyl)-  
 (9CI) (CA INDEX NAME)]



L34 ANSWER 8 OF 19 HCAPLUS COPYRIGHT 2003 ACS  
 AN 1997:595405 HCAPLUS  
 DN 127:292927  
 TI Improved functional group compatibility in the palladium-catalyzed amination of aryl bromides  
 AU Wolfe, John P.; Buchwald, Stephen L.  
 CS Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA, 02139, USA  
 SO Tetrahedron Letters (1997), 38(36), 6359-6362  
 CODEN: TELEAY; ISSN: 0040-4039  
 PB Elsevier  
 DT Journal  
 LA English  
 CC 25-4 (Benzene, Its Derivatives, and Condensed Benzenoid Compounds)  
 OS CASREACT 127:292927  
 AB Aryl bromides are coupled with amines in the presence of a Pd catalyst and a stoichiometric amt. of Cs carbonate. Using these conditions base-sensitive functional groups, which were incompatible with the authors' previously reported catalytic amination reaction conditions, are well tolerated.  
 ST palladium catalyst amination aryl bromide; amine prepn  
 IT Amination  
 Amination catalysts  
 (improved functional group compatibility in palladium-catalyzed amination of aryl bromides)  
 IT Aryl bromides  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (improved functional group compatibility in palladium-catalyzed amination of aryl bromides)  
 IT Amines, preparation  
 RL: SPN (Synthetic preparation); PREP (Preparation)  
 (improved functional group compatibility in palladium-catalyzed amination of aryl bromides)  
 IT 3375-31-3, Palladium diacetate 51364-51-3, Tris(dibenzylideneacetone)dipalladium 98327-87-8, BINAP 197241-39-7  
 RL: CAT (Catalyst use); USES (Uses)  
 (improved functional group compatibility in palladium-catalyzed amination of aryl bromides)  
 IT 99-90-1 100-46-9, Benzylamine, reactions 100-61-8, reactions 103-67-3, N-Methylbenzylamine 104-92-7, 4-Bromoanisole 104-94-9, 4-Methoxyaniline 106-49-0, 4-Methylaniline, reactions 110-89-4, Piperidine, reactions 110-91-8, Morpholine, reactions 111-26-2,

1-Aminohexane 111-92-2 123-75-1, Pyrrolidine, reactions 553-94-6,  
 2-Bromo-1,4-dimethylbenzene 586-78-7, 4-Bromonitrobenzene 610-94-6,  
 Methyl 2-bromobenzoate 618-89-3, Methyl 3-bromobenzoate 619-42-1,  
 Methyl 4-bromobenzoate 623-00-7, 4-Bromocyanobenzene 1122-91-4,  
 4-Bromobenzaldehyde 2038-03-1, 4-(2-Aminoethyl)morpholine 3972-65-4,  
 4-tert-Butyl-1-bromobenzene 5798-75-4, Ethyl 4-bromobenzoate  
 40371-64-0 154607-01-9, 4-Bromo-2-chlorobenzonitrile

RL: RCT (Reactant); RACT (Reactant or reagent)  
 (improved functional group compatibility in palladium-catalyzed  
 amination of aryl bromides)

IT 1204-85-9P 1215-41-4P 6574-15-8P 21971-24-4P 23600-89-7P  
 27347-14-4P 65213-46-9P 97053-04-8P 101038-65-7P 158833-49-9P  
 185259-34-1P 188026-55-3P 197172-65-9P 197172-67-1P 197172-69-3P

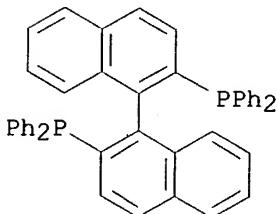
197173-65-2P 197173-66-3P 197173-67-4P  
 RL: SPN (Synthetic preparation); PREP (Preparation)  
 (prepn. of)

IT 98327-87-8, BINAP

RL: CAT (Catalyst use); USES (Uses)  
 (improved functional group compatibility in palladium-catalyzed  
 amination of aryl bromides)

RN 98327-87-8 HCAPLUS

CN Phosphine, [1,1'-binaphthalene]-2,2'-diylbis[diphenyl- (9CI) (CA INDEX  
 NAME)]



L34 ANSWER 9 OF 19 HCAPLUS COPYRIGHT 2003 ACS

AN 1997:565069 HCAPLUS

DN 127:205161

TI Palladium-Catalyzed Coupling of Optically Active Amines with Aryl Bromides

AU Wagaw, Seble; Rennels, Roger A.; Buchwald, Stephen L.

CS Department of Chemistry, Massachusetts Institute of Technology, Cambridge,  
 MA, 02139, USA

SO Journal of the American Chemical Society (1997), 119(36),  
 8451-8458

CODEN: JACSAT; ISSN: 0002-7863

PB American Chemical Society

DT Journal

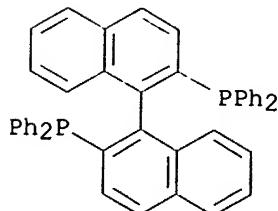
LA English

CC 21-2 (General Organic Chemistry)

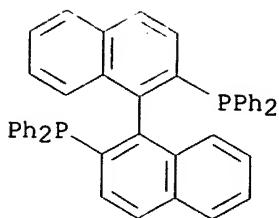
OS CASREACT 127:205161

AB The coupling of enantiomerically enriched amines with aryl bromides produces the corresponding N-aryl derivs. The choice of ligand in the palladium-catalyzed coupling is crit. to the formation of the anilines without loss of enantiomeric purity. While LnPd [L = P(o-tolyl)3] successfully catalyzes the intramol. aryl amination of .alpha.-substituted optically pure amines, intermol. coupling reactions with this catalyst system gives racemized products. In contrast, intermol. N-arylations employing LnPd [L = (.+-.)-BINAP] gives products in good yields with no erosion of enantiopurity. A mechanism for the obsd. racemization is proposed. The utility of the intramol. process is demonstrated by the synthesis of 3, an intermediate in the formal synthesis of 4, a potent ACE inhibitor.

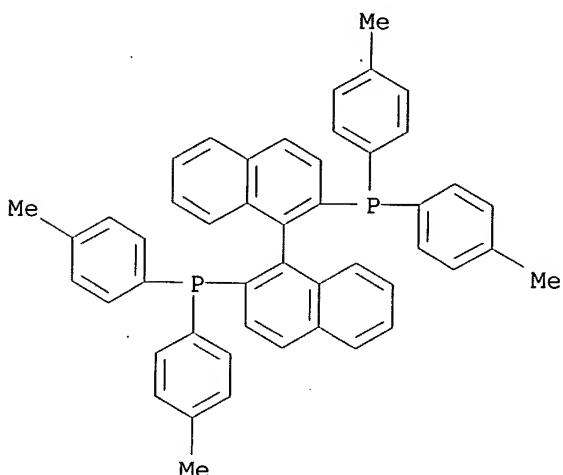
ST palladium catalyst coupling amine aryl bromide  
 IT Coupling reaction catalysts  
 Stereochemistry  
     (palladium-catalyzed coupling of optically active amines with aryl bromides)  
 IT Amines, reactions  
 Aryl bromides  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
     (palladium-catalyzed coupling of optically active amines with aryl bromides)  
 IT 603-35-0, Triphenylphosphine, uses 3375-31-3, Palladium diacetate  
 3411-48-1, Tris(1-naphthyl)phosphine 4731-65-1, Tris(o-methoxyphenyl)phosphine 6163-58-2, Tris(o-methylphenyl)phosphine 12150-46-8, DPPF 51364-51-3 72287-26-4 98327-87-8, BINAP 99326-34-8 136779-28-7  
 RL: CAT (Catalyst use); USES (Uses)  
     (palladium-catalyzed coupling of optically active amines with aryl bromides)  
 IT 82924-03-6P  
 RL: PNU (Preparation, unclassified); PREP (Preparation)  
     (palladium-catalyzed coupling of optically active amines with aryl bromides)  
 IT 90-90-4, 4-Bromobenzophenone 92-66-0, 4-Bromobiphenyl 106-39-8  
 109-04-6, 2-Bromopyridine 115-11-7, Isobutylene, reactions 402-43-7  
 513-49-5 580-13-2, 2-Bromonaphthalene 583-55-1, o-Iodobromobenzene  
 628-20-6, 4-Chlorobutyronitrile 3182-95-4, (S)-Phenylalaninol  
 3886-69-9, (R)-.alpha.-Methylbenzylamine 4165-57-5, Bromobenzene-d5  
 5913-13-3 5933-40-4 17789-14-9 18698-97-0, 2-Bromophenylacetic acid  
 20439-47-8 23356-96-9, (S)-Prolinol 35356-70-8 59347-91-0,  
 (S)-2-Phenylpyrrolidine  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
     (palladium-catalyzed coupling of optically active amines with aryl bromides)  
 IT 154261-30-0P 194723-99-4P 194724-01-1P 194724-02-2P 194724-09-9P  
 194724-26-0P  
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)  
     (palladium-catalyzed coupling of optically active amines with aryl bromides)  
 IT 110592-39-7P 194724-00-0P 194724-03-3P 194724-04-4P 194724-10-2P  
 194724-13-5P 194724-16-8P 194724-18-0P 194724-20-4P 194724-22-6P  
 194724-24-8P 194724-25-9P  
 RL: SPN (Synthetic preparation); PREP (Preparation)  
     (palladium-catalyzed coupling of optically active amines with aryl bromides)  
 IT 98327-87-8, BINAP  
 RL: CAT (Catalyst use); USES (Uses)  
     (palladium-catalyzed coupling of optically active amines with aryl bromides)  
 RN 98327-87-8 HCAPLUS  
 CN Phosphine, [1,1'-binaphthalene]-2,2'-diylbis[diphenyl- (9CI) (CA INDEX NAME)



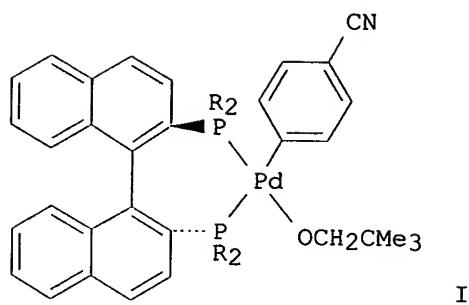
L34 ANSWER 10 OF 19 HCAPLUS COPYRIGHT 2003 ACS  
 AN 1997:559636 HCAPLUS  
 DN 127:262475  
 TI Room temperature catalytic amination of aryl iodides  
 AU Wolfe, John P.; Buchwald, Stephen L.  
 CS Department Chemistry, Massachusetts Institute Technology, Cambridge, MA,  
 02139, USA  
 SO Journal of Organic Chemistry (1997), 62(17), 6066-6068  
 CODEN: JOCEAH; ISSN: 0022-3263  
 PB American Chemical Society  
 DT Journal  
 LA English  
 CC 25-4 (Benzene, Its Derivatives, and Condensed Benzenoid Compounds)  
 OS CASREACT 127:262475  
 AB Mixts. of Pd2(dba)3 and BINAP or Tol-BINAP catalyze the coupling of aryl iodides with aliph. amines in the presence of stoichiometric amts. of NaOBu-t and 18-Crown-6 at room temp. in good to excellent yields. Anilines may be coupled with aryl iodides under similar conditions at 40 .degree.C in good yields. For example, the amination of 1-iodo-4-methylbenzene with piperidine gave 1-(4-methylphenyl)piperidine in 85% yield.  
 ST amination aryl iodide amine; benzenamine phenyl prep; phenylmorpholine phenylpiperidine prep  
 IT Iodides, reactions  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (arom.; room temp. catalytic amination of aryl iodides)  
 IT Amination  
 (room temp. catalytic amination of aryl iodides)  
 IT 620-84-8P 22148-20-5P 54660-04-7P, N-(4-Methoxyphenyl)pyrrolidine  
 65489-12-5P 84736-47-0P 87698-82-6P 97053-04-8P 174307-98-3P  
 196213-26-0P 196213-27-1P  
 RL: SPN (Synthetic preparation); PREP (Preparation)  
 (prep. of)  
 IT 51364-51-3, Tris(dibenzylideneacetone)dipalladium 76189-56-5,  
 (S)-BINAP 99646-28-3  
 RL: CAT (Catalyst use); USES (Uses)  
 (room temp. catalytic amination of aryl iodides)  
 IT 62-53-3, Benzenamine, reactions 95-53-4, 2-Methylaniline, reactions  
 100-61-8, N-Methylaniline, reactions 104-94-9, 4-Methoxyaniline  
 110-89-4, Piperidine, reactions 110-91-8, Morpholine, reactions  
 111-26-2, 1-Hexanamine 123-75-1, Pyrrolidine, reactions 583-55-1,  
 1-Bromo-2-iodobenzene 589-87-7, 1-Bromo-4-iodobenzene 591-18-4,  
 1-Bromo-3-iodobenzene 624-31-7, 1-Iodo-4-methylbenzene 696-62-8,  
 1-Iodo-4-methoxybenzene 865-48-5, Sodium tert-butoxide 1122-42-5,  
 2-Iodo-1,4-dimethylbenzene 35779-04-5 77350-52-8, N,N-Diethyl-4-  
 iodobenzamide  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (room temp. catalytic amination of aryl iodides)  
 IT 31053-03-9P  
 RL: SPN (Synthetic preparation); PREP (Preparation)  
 (room temp. catalytic amination of aryl iodides)  
 IT 76189-56-5, (S)-BINAP 99646-28-3  
 RL: CAT (Catalyst use); USES (Uses)  
 (room temp. catalytic amination of aryl iodides)  
 RN 76189-56-5 HCAPLUS  
 CN Phosphine, (1S)-[1,1'-binaphthalene]-2,2'-diylbis[diphenyl- (9CI) (CA INDEX NAME)



RN 99646-28-3 HCAPLUS  
 CN Phosphine, (1R)-[1,1'-binaphthalene]-2,2'-diylbis[bis(4-methylphenyl)-  
 (9CI) (CA INDEX NAME)]



L34 ANSWER 11 OF 19 HCAPLUS COPYRIGHT 2003 ACS  
 AN 1997:457099 HCAPLUS  
 DN 127:135936  
 TI Direct Observation of C-O Reductive Elimination from Palladium Aryl Alkoxide Complexes To Form Aryl Ethers  
 AU Widenhoefer, Ross A.; Zhong, H. Annita; Buchwald, Stephen L.  
 CS Department of Chemistry, Massachusetts Institute of Technology, Cambridge,  
 MA, 02139, USA  
 SO Journal of the American Chemical Society (1997), 119(29),  
 6787-6795  
 CODEN: JACSAT; ISSN: 0002-7863  
 PB American Chemical Society  
 DT Journal  
 LA English  
 CC 29-13 (Organometallic and Organometalloidal Compounds)  
 Section cross-reference(s): 22  
 OS CASREACT 127:135936  
 GI



AB Reaction of KOCH<sub>2</sub>CMe<sub>3</sub> with [(R)-Tol-BINAP]Pd(p-C<sub>6</sub>H<sub>4</sub>CN)Br formed [(R)-Tol-BINAP]Pd(p-C<sub>6</sub>H<sub>4</sub>CN)(OCH<sub>2</sub>CMe<sub>3</sub>) I (5; R = p-tolyl) in quant. yield (1H NMR spectroscopy). Thermolysis of 5 in THF-d<sub>8</sub> at 47.degree. led to C-O reductive elimination with formation of p-neopentoxybenzonitrile (85 .+- . 2%). A secondary P-C bond-cleavage process gave 4,4'-dimethylbiphenyl (16 .+- . 2%). Kinetic anal. of the decompn. of 5 at 47.degree. in the presence of excess K neopentoxyde established the two-term rate law, rate = k[5] + k'[5][KOC<sub>2</sub>CMe<sub>3</sub>], where k = 1.50 .+- . 0.07 .times. 10<sup>-3</sup> s<sup>-1</sup> and k' = 6.2 .+- . 0.4 .times. 10<sup>-3</sup> s<sup>-1</sup> M<sup>-1</sup>, consistent with reductive elimination via competing alkoxide-dependent and alkoxide-independent pathways. Excess KOCH<sub>2</sub>CMe<sub>3</sub> exchanged rapidly with the Pd-bound alkoxide ligand of 5 at 47.degree. according to the rate law: rate exchange = k<sub>ex</sub>[5][KOC<sub>2</sub>CMe<sub>3</sub>], where k<sub>ex</sub> = 1.0 .+- . 0.1 .times. 10<sup>2</sup> s<sup>-1</sup> M<sup>-1</sup>. Thermolysis of the related Pd p-cyanophenyl alkoxide complexes (P-P)Pd(p-C<sub>6</sub>H<sub>4</sub>CN)(OR) [P-P = (S)-BINAP, R = CH<sub>2</sub>CMe<sub>3</sub>; P-P = (R)-Tol-BINAP, R = CHMe<sub>2</sub>, CMe<sub>3</sub>; P-P = 1,1'-bis(diphenylphosphino)ferrocene (dpff), R = CH<sub>2</sub>CMe<sub>3</sub>, CMe<sub>3</sub>] and (dpff)Pd[o-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>2</sub>C(Me)<sub>2</sub>O] led to aryl ether formation in 46-91% yield.

ST aryl ether prepn; palladium aryl alkoxide prepn reductive elimination; thermal decompn palladium aryl alkoxide kinetics

IT Ethers, preparation  
RL: SPN (Synthetic preparation); PREP (Preparation)  
(arom.; formation of aryl ethers by reductive elimination from palladium aryl alkoxide complexes)

IT Bond formation  
(carbon-oxygen; in formation of aryl ethers by reductive elimination from palladium aryl alkoxide complexes)

IT Linear free energy relationship  
(for kinetics of thermal decompn. of palladium aryl alkoxide complexes)

IT Thermal decomposition kinetics  
(kinetics of thermal décompr. of palladium aryl alkoxide complexes)

IT Elimination reaction, coordinative  
(reductive; reductive elimination from palladium aryl alkoxide complexes)

IT 92-52-4P, Biphenyl, preparation 100-47-0P, Benzonitrile, preparation 613-33-2P, 4,4'-Dimethylbiphenyl 630-19-3P, Pivaldehyde 644-08-6P, 4-Methylbiphenyl 79615-68-2P 91949-95-0P 185259-36-3P  
RL: SPN (Synthetic preparation); PREP (Preparation)  
(formation of aryl ethers by reductive elimination from palladium aryl alkoxide complexes)

IT 193001-21-7P 193001-23-9P 193001-25-1P 193001-27-3P 193001-29-5P  
193001-31-9P 193001-33-1P 193001-36-4P  
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)  
(prepn. and kinetics of thermal decompn. of palladium aryl alkoxide complexes)

IT 623-00-7, 4-Bromobenzonitrile 865-47-4, Potassium tert-butoxide 1192-96-7, Potassium p-cresolate 3058-39-7, 4-Iodobenzonitrile

6163-58-2, Tri-o-tolylphosphine 6831-82-9, Potassium isopropoxide  
 12150-46-8, 1,1'-Bis(diphenylphosphino)ferrocene 51364-51-3  
 55553-85-0, Potassium neopentoxide 76189-56-5 99646-28-3  
**100165-88-6** 183864-59-7

RL: RCT (Reactant); RACT (Reactant or reagent)  
 (prepn. of palladium aryl alkoxide complexes)

IT 193001-13-7P 193001-15-9P 193001-17-1P 193001-19-3P 193001-39-7P  
 193001-41-1P

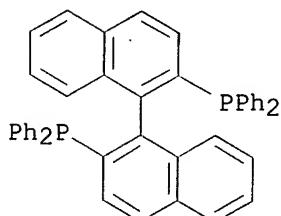
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT  
 (Reactant or reagent)  
 (prepn. of palladium aryl alkoxide complexes)

IT 1198-96-5P  
 RL: SPN (Synthetic preparation); PREP (Preparation)  
 (thermal decompn. of palladium aryl alkoxide complexes)

IT **76189-56-5** 99646-28-3 **100165-88-6**  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (prepn. of palladium aryl alkoxide complexes)

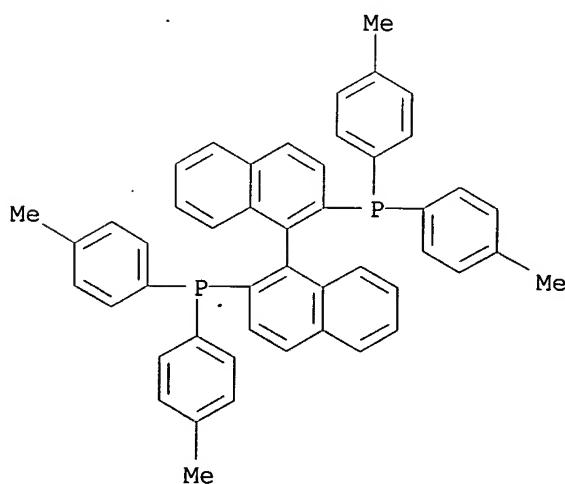
RN 76189-56-5 HCPLUS

CN Phosphine, (1S)-[1,1'-binaphthalene]-2,2'-diylbis[diphenyl- (9CI) (CA INDEX NAME)



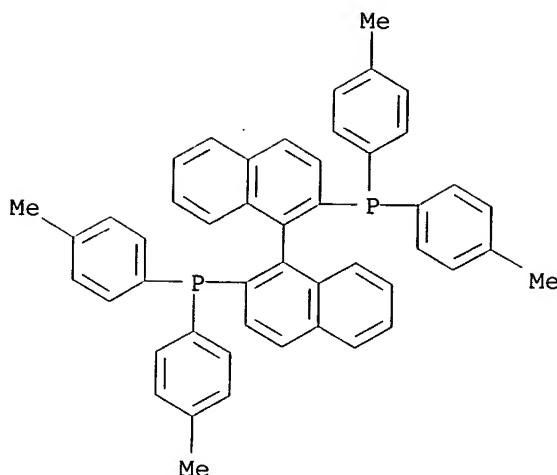
RN 99646-28-3 HCPLUS

CN Phosphine, (1R)-[1,1'-binaphthalene]-2,2'-diylbis[bis(4-methylphenyl)- (9CI) (CA INDEX NAME)



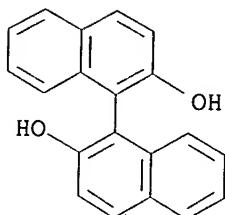
RN 100165-88-6 HCPLUS

CN Phosphine, (1S)-[1,1'-binaphthalene]-2,2'-diylbis[bis(4-methylphenyl)- (9CI) (CA INDEX NAME)



L34 ANSWER 12 OF 19 HCAPLUS COPYRIGHT 2003 ACS  
 AN 1997:226494 HCAPLUS  
 DN 126:199628  
 TI Improved Procedure for the Preparation of Enantiomerically Pure Ethylenebis(tetrahydroindenyl)zirconium Derivatives  
 AU Chin, Bain; Buchwald, Stephen L.  
 CS Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA, MASSACHUSETTS 02139, USA  
 SO Journal of Organic Chemistry (1997), 62(7), 2267-2268  
 CODEN: JOCEAH; ISSN: 0022-3263  
 PB American Chemical Society  
 DT Journal  
 LA English  
 CC 29-10 (Organometallic and Organometalloidal Compounds)  
 OS CASREACT 126:199628  
 AB Enantiomerically pure complexes (R,R)-ethylenebis(tetrahydroindenyl) Zr(R)-1,1'-binaphth-2,2'-diolate and (S,S)-ethylenebis(tetrahydroindenyl) Zr(S)-1,1'-biphen-2,2'-diolate (1d) were prep'd. from (rac)- ethylenebis(tetrahydroindenyl)zirconium dichloride (1a) and (R)-1,1'-binaphth-2,2'-diol. The enantiomer of 1a that did not form a binaphthdiolate complex was sepd. as an ethylenebis(tetrahydroindenyl)zirconium bis(4-aminobenzoate) complex and then converted to 1d.  
 ST enantiomer ethylenebistetrahydroindenyl zirconium complex prep'n; indenyl ethylenebistetrahydro zirconium complex enantiomer prep'n  
 IT Enantiomers  
 .(improved procedure for prep'n. of enantiomerically pure ethylene(tetrahydroindenyl)zirconium derivs.)  
 IT Metallocenes  
 RL: SPN (Synthetic preparation); PREP (Preparation)  
 (zirconocenes; improved procedure for prep'n. of enantiomerically pure ethylene(tetrahydroindenyl)zirconium derivs.)  
 IT 150-13-0, 4-Aminobenzoic acid 1806-29-7, 1,1'-Biphen-2-ol  
 18531-94-7, (R)-1,1'-Binaphth-2,2'-diol 100163-29-9  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (improved procedure for prep'n. of enantiomerically pure ethylene(tetrahydroindenyl)zirconium derivs.)  
 IT 187661-02-5P  
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)  
 (improved procedure for prep'n. of enantiomerically pure ethylene(tetrahydroindenyl)zirconium derivs.)  
 IT 115857-04-0P 115938-35-7P 123236-85-1P 187757-13-7P

IT RL: SPN (Synthetic preparation); PREP (Preparation)  
 (improved procedure for prepn. of enantiomerically pure  
 ethylene(tetrahydroindenyl)zirconium derivs.)  
**18531-94-7, (R)-1,1'-Binaphth-2,2'-diol**  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (improved procedure for prepn. of enantiomerically pure  
 ethylene(tetrahydroindenyl)zirconium derivs.)  
 RN 18531-94-7 HCPLUS  
 CN [1,1'-Binaphthalene]-2,2'-diol, (1R)- (9CI) (CA INDEX NAME)



L34 ANSWER 13 OF 19 HCPLUS COPYRIGHT 2003 ACS  
 AN 1997:195810 HCPLUS  
 DN 126:250954  
 TI Palladium-Catalyzed Intermolecular Carbon-Oxygen Bond Formation: A New  
 Synthesis of Aryl Ethers  
 AU Palucki, Michael; Wolfe, John P.; Buchwald,  
 Stephen L.  
 CS Department of Chemistry, Massachusetts Institute of Technology, Cambridge,  
 MA, 02139, USA  
 SO Journal of the American Chemical Society (1997), 119(14),  
 3395-3396  
 CODEN: JACSAT; ISSN: 0002-7863  
 PB American Chemical Society  
 DT Journal  
 LA English  
 CC 25-9 (Benzene, Its Derivatives, and Condensed Benzenoid Compounds)  
 OS CASREACT 126:250954  
 AB The synthesis of aryl ethers by the intermol. formation of a carbon-oxygen  
 bond can be catalyzed by a combination of Pd2(dba)3 or Pd(OAc)2 and  
 Tol-BINAP in toluene. This process yields aryl ethers in moderate to good  
 yields. While little or no conversion is seen in control reactions run in  
 toluene, it was found for some electron-poor aryl bromides that  
 nucleophilic arom. substitution could be carried out in DMF in the absence  
 of metal catalyst under mild conditions.  
 ST palladium catalyst substitution bromoarene alc; aryl ether prepn  
 IT Ethers, preparation  
 RL: SPN (Synthetic preparation); PREP (Preparation)  
 (arom.; prepn. of aryl ethers by palladium-catalyzed reaction of aryl  
 bromides and alcs.)  
 IT Substitution reaction, nucleophilic  
 (arom.; uncatalyzed and palladium-catalyzed reaction of aryl bromides  
 and alcs.)  
 IT Bond formation  
 (carbon-oxygen; palladium-catalyzed carbon-oxygen bond formation)  
 IT Substitution reaction catalysts  
 (nucleophilic, arom.; uncatalyzed and palladium-catalyzed reaction of  
 aryl bromides and alcs.)  
 IT Alcohols, reactions  
 Aryl bromides  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (prep. of aryl ethers by palladium-catalyzed reaction of aryl bromides)

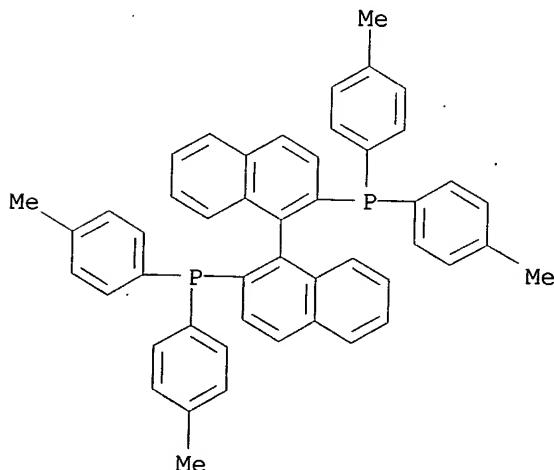
and alcs.)  
IT 3375-31-3, Palladium diacetate 51364-51-3, Tris(dibenzylideneacetone)dipalladium 99646-28-3 100165-88-6  
RL: CAT (Catalyst use); USES (Uses)  
(prepn. of aryl ethers by palladium-catalyzed reaction of aryl bromides and alcs.)

IT 67-56-1, Methanol, reactions 67-63-0, 2-Propanol, reactions 90-11-9,  
1-Bromonaphthalene 96-41-3, Cyclopentanol 98-85-1, sec-Phenethyl alcohol 100-51-6, Benzyl alcohol, reactions 108-93-0, Cyclohexanol, reactions 402-43-7 584-02-1, 3-Pentanol 623-00-7, p-Bromobenzonitrile 865-48-5, Sodium tert-butoxide 1564-64-3, 9-Bromoanthracene 2081-44-9 2216-51-5, (-)-Menthol 3972-65-4 154607-01-9  
RL: RCT (Reactant); RACT (Reactant or reagent)  
(prepn. of aryl ethers by palladium-catalyzed reaction of aryl bromides and alcs.)

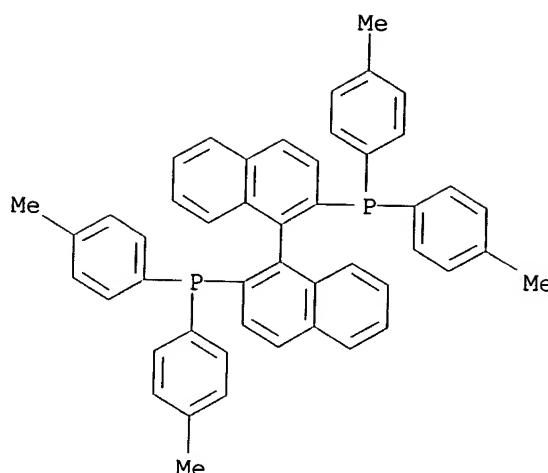
IT 874-90-8P 21571-62-0P 31603-95-9P 52805-36-4P 91949-95-0P  
188527-52-8P 188527-54-0P 188527-60-8P 188527-62-0P 188527-64-2P  
188527-66-4P 188527-68-6P 188527-70-0P 188527-72-2P  
RL: SPN (Synthetic preparation); PREP (Preparation)  
(prepn. of aryl ethers by palladium-catalyzed reaction of aryl bromides and alcs.)

IT 99646-28-3 100165-88-6  
RL: CAT (Catalyst use); USES (Uses)  
(prepn. of aryl ethers by palladium-catalyzed reaction of aryl bromides and alcs.)

RN 99646-28-3 HCPLUS  
CN Phosphine, (1R)-[1,1'-binaphthalene]-2,2'-diylbis[bis(4-methylphenyl)- (9CI) (CA INDEX NAME)



RN 100165-88-6 HCPLUS  
CN Phosphine, (1S)-[1,1'-binaphthalene]-2,2'-diylbis[bis(4-methylphenyl)- (9CI) (CA INDEX NAME)]

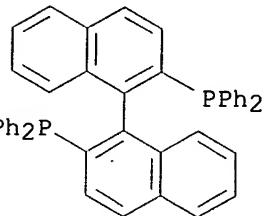


L34 ANSWER 14 OF 19 HCAPLUS COPYRIGHT 2003 ACS  
 AN 1997:164910 HCAPLUS  
 DN 126:143782  
 TI Palladium-Catalyzed Amination of Aryl Triflates  
 AU Wolfe, John P.; Buchwald, Stephen L.  
 CS Department of Chemistry, Massachusetts Institute of Technology, Cambridge,  
 MA, 02139, USA  
 SO Journal of Organic Chemistry (1997), 62(5), 1264-1267  
 CODEN: JOCEAH; ISSN: 0022-3263  
 PB American Chemical Society  
 DT Journal  
 LA English  
 CC 21-2 (General Organic Chemistry)  
 OS CASREACT 126:143782  
 AB The conversion of aryl triflates to the corresponding aniline derivs. was accomplished in moderate to good yield using a catalyst consisting of the combination of palladium acetate (2 mol %) and either BINAP or Tol-BINAP. In contrast to the corresponding palladium-catalyzed amination of aryl bromides and iodides, electronically neutral aryl triflates gave higher yields of arylamines than did electron deficient aryl triflates, presumably due to the increased rate of base-promoted triflate cleavage in electron deficient substrates.  
 ST palladium catalyst amination aryl triflate  
 IT Amination  
 Amination catalysts  
     (palladium-catalyzed amination of aryl triflates)  
 IT 3375-31-3, Palladium diacetate 51364-51-3, Tris(dibenzylideneacetone)dipalladium 76189-55-4, (R)-BINAP 76189-56-5, (S)-BINAP 99646-28-3 100165-88-6  
 RL: CAT (Catalyst use); USES (Uses)  
     (palladium-catalyzed amination of aryl triflates)  
 IT 62-53-3, Aniline, reactions 103-67-3, N-Methylbenzylamine 109-01-3, 1-Methylpiperazine 109-73-9, Butylamine, reactions 110-89-4, Piperidine, reactions 110-91-8, Morpholine, reactions 111-26-2, Hexylamine 123-75-1, Pyrrolidine, reactions 177-11-7, 1,4-Dioxa-8-azaspiro[4.5]decane 66107-29-7 66107-32-2 87241-52-9 99747-74-7, 1-Naphthyl triflate 109586-43-8 124643-34-1 154318-75-9  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
     (palladium-catalyzed amination of aryl triflates)  
 IT 90-30-2P 10282-31-2P 24758-49-4P 54660-04-7P 66797-55-5P 81506-14-1P 114849-77-3P 151696-67-2P 185259-34-1P 186682-66-6P 186682-67-7P 186682-68-8P 186682-69-9P 186682-70-2P 186682-71-3P

IT RL: SPN (Synthetic preparation); PREP (Preparation)  
 (palladium-catalyzed amination of aryl triflates)  
 76189-55-4, (R)-BINAP 76189-56-5, (S)-BINAP  
 99646-28-3 100165-88-6  
 RL: CAT (Catalyst use); USES (Uses)  
 (palladium-catalyzed amination of aryl triflates)

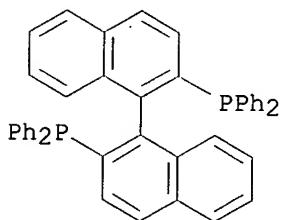
RN 76189-55-4 HCPLUS

CN Phosphine, (1R)-[1,1'-binaphthalene]-2,2'-diylbis[diphenyl- (9CI) (CA INDEX NAME)]



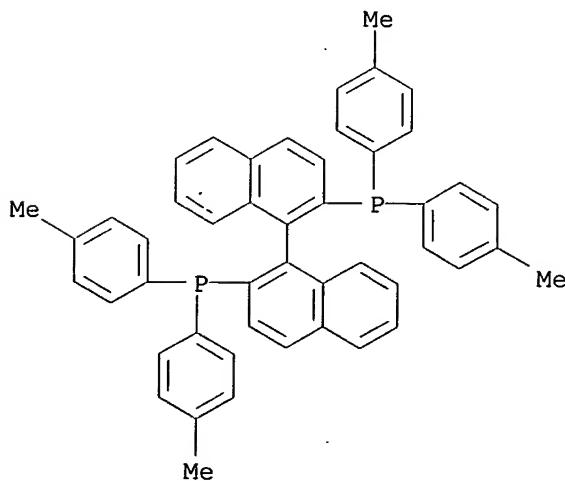
RN 76189-56-5 HCPLUS

CN Phosphine, (1S)-[1,1'-binaphthalene]-2,2'-diylbis[diphenyl- (9CI) (CA INDEX NAME)]



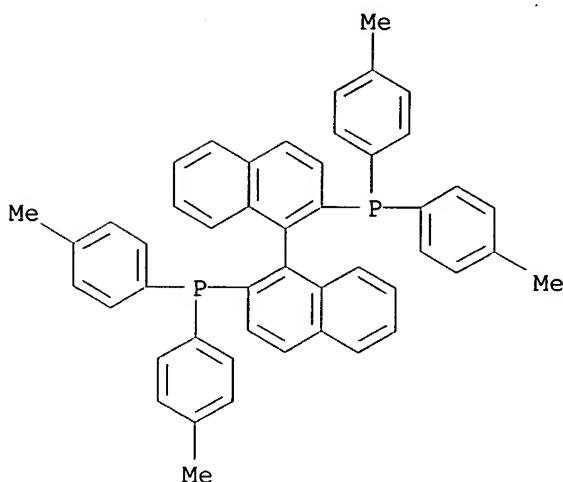
RN 99646-28-3 HCPLUS

CN Phosphine, (1R)-[1,1'-binaphthalene]-2,2'-diylbis[bis(4-methylphenyl)- (9CI) (CA INDEX NAME)]



RN 100165-88-6 HCPLUS

CN Phosphine, (1S)-[1,1'-binaphthalene]-2,2'-diylbis[bis(4-methylphenyl)- (9CI) (CA INDEX NAME)]



L34 ANSWER 15 OF 19 HCPLUS COPYRIGHT 2003 ACS  
 AN 1996:618987 HCPLUS  
 DN 125:328464  
 TI The Synthesis of Aminopyridines: A Method Employing Palladium-Catalyzed Carbon-Nitrogen Bond Formation  
 AU Wagaw, Seble; Buchwald, Stephen L.  
 CS Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA, 02139, USA  
 SO Journal of Organic Chemistry (1996), 61(21), 7240-7241  
 CODEN: JOCEAH; ISSN: 0022-3263  
 PB American Chemical Society  
 DT Journal  
 LA English  
 CC 27-16 (Heterocyclic Compounds (One Hetero Atom))  
 OS CASREACT 125:328464  
 AB Aminopyridines are efficiently synthesized under mild conditions by the cross coupling reaction of 2-, 3-, and 4-bromopyridines with primary and secondary amines utilizing palladium(0) complexes with chelating bis(phosphine) ligands. A variety of aminopyridines were prepd. including mono-, di-, tri-, and tetra-pyridinylated products.  
 ST aminopyridine prep; pyridine amino prep; cross coupling bromopyridine amine  
 IT Amines, reactions  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (prep. of aminopyridines by palladium-catalyzed cross coupling of bromopyridines with amines)  
 IT Coupling reaction  
 Coupling reaction catalysts  
 (cross-, prep. of aminopyridines by palladium-catalyzed cross coupling of bromopyridines with amines)  
 IT 3375-31-3, Palladium diacetate 6737-42-4, Dppp 51364-51-3  
 98327-87-8, BINAP  
 RL: CAT (Catalyst use); USES (Uses)  
 (prep. of aminopyridines by palladium-catalyzed cross coupling of bromopyridines with amines)  
 IT 62-53-3, Aniline, reactions 100-61-8, N-Methylaniline, reactions 103-67-3, N-Methylbenzylamine 108-91-8, Cyclohexylamine, reactions 109-04-6, 2-Bromopyridine 109-09-1, 2-Chloropyridine 109-76-2, 1,3-Diaminopropane 110-91-8, Morpholine, reactions 111-26-2, Hexylamine 504-29-0, 2-Aminopyridine 626-05-1, 2,6-Dibromopyridine 626-55-1, 3-Bromopyridine 1121-22-8, trans-1,2-Diaminocyclohexane

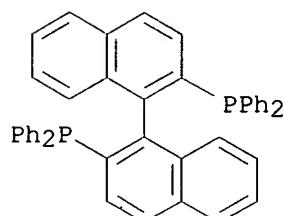
5332-24-1, 3-Bromoquinoline 19524-06-2, 4-Bromopyridine hydrochloride  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (prepn. of aminopyridines by palladium-catalyzed cross coupling of  
 bromopyridines with amines)

IT 1202-34-2P 2767-91-1P 5051-97-8P 15513-16-3P 20173-75-5P  
 24255-25-2P 32405-79-1P 64690-14-8P 92670-29-6P 100051-12-5P  
 183135-50-4P 183135-51-5P 183135-52-6P 183135-53-7P 183135-54-8P  
 183135-55-9P 183135-56-0P  
 RL: SPN (Synthetic preparation); PREP (Preparation)  
 (prepn. of aminopyridines by palladium-catalyzed cross coupling of  
 bromopyridines with amines)

IT 98327-87-8, BINAP  
 RL: CAT (Catalyst use); USES (Uses)  
 (prepn. of aminopyridines by palladium-catalyzed cross coupling of  
 bromopyridines with amines)

RN 98327-87-8 HCAPLUS

CN Phosphine, [1,1'-binaphthalene]-2,2'-diylbis[diphenyl- (9CI) (CA INDEX NAME)]



L34 ANSWER 16 OF 19 HCAPLUS COPYRIGHT 2003 ACS  
 AN 1996:616752 HCAPLUS  
 DN 126:7946  
 TI Synthesis of Oxygen Heterocycles via a Palladium-Catalyzed C-O  
 Bond-Forming Reaction  
 AU Palucki, Michael; Wolfe, John P.; Buchwald,  
 Stephen L.  
 CS Department of Chemistry, Massachusetts Institute of Technology, Cambridge,  
 MA, 02139, USA  
 SO Journal of the American Chemical Society (1996), 118(42),  
 10333-10334  
 CODEN: JACSAT; ISSN: 0002-7863  
 PB American Chemical Society  
 DT Journal  
 LA English  
 CC 27-13 (Heterocyclic Compounds (One Hetero Atom))  
 OS CASREACT 126:7946  
 AB The synthesis of oxygen heterocycles was accomplished via a  
 palladium-catalyzed intramol. ipso substitution of an aryl halide with an  
 alc. The use of chelating bis(phosphine) ligands and a suitable base was  
 found to be crucial for achieving good yields of cyclized products. The  
 reaction was found to have a reasonable degree of functional group  
 compatibility and can be used for the formation of five-, six-, and  
 seven-membered oxygen heterocycles. (DPPF)Pd(Br)[2-(2-methyl-2-  
 butanol)benzene] [DPPF = 1,1'-bis(diphenylphosphino)ferrocene] was  
 isolated, characterized and found to be chem. and kinetically competent as  
 an intermediate in the proposed catalytic cycle.  
 ST palladium catalyst intramol coupling haloarene alc; cyclization aryl  
 halide alc; bond formation carbon oxygen  
 IT Bond formation  
 (carbon-oxygen; prepn. of oxygen heterocycles by palladium catalyzed  
 intramol. coupling of aryl halides with alcs.)

IT Cross-coupling reaction  
 Cyclocondensation reaction  
 (prepn. of oxygen heterocycles by palladium catalyzed intramol.  
 coupling of aryl halides with alcs.)

IT Cross-coupling reaction catalysts  
 RL: CAT (Catalyst use); USES (Uses)  
 (prepn. of oxygen heterocycles by palladium catalyzed intramol.  
 coupling of aryl halides with alcs.)

IT 1198-96-5P 6337-33-3P 13030-26-7P 124773-73-5P 183864-52-0P  
 183864-53-1P 183864-54-2P 183864-55-3P 183864-56-4P 183864-57-5P  
 183864-58-6P  
 RL: SPN (Synthetic preparation); PREP (Preparation)  
 (prepn. of)

IT 3375-31-3, Palladium diacetate 7440-05-3, Palladium, uses 12150-46-8,  
 1,1'-Bis(diphenylphosphino)ferrocene 76189-56-5,  
 (S)-(-)-2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl 100165-88-6  
 RL: CAT (Catalyst use); USES (Uses)  
 (prepn. of oxygen heterocycles by palladium catalyzed intramol.  
 coupling of aryl halides with alcs.)

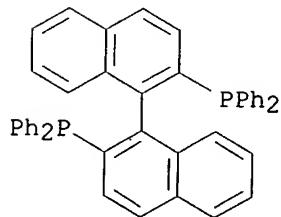
IT 67130-96-5 126495-44-1 142569-52-6 183864-38-2 183864-40-6  
 183864-42-8 183864-44-0 183864-45-1 183864-47-3 183864-49-5  
 183864-50-8 183864-51-9  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (prepn. of oxygen heterocycles by palladium catalyzed intramol.  
 coupling of aryl halides with alcs.)

IT 183864-59-7P  
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT  
 (Reactant or reagent)  
 (prepn. of oxygen heterocycles by palladium catalyzed intramol.  
 coupling of aryl halides with alcs.)

IT 76189-56-5, (S)-(-)-2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl  
 100165-88-6  
 RL: CAT (Catalyst use); USES (Uses)  
 (prepn. of oxygen heterocycles by palladium catalyzed intramol.  
 coupling of aryl halides with alcs.)

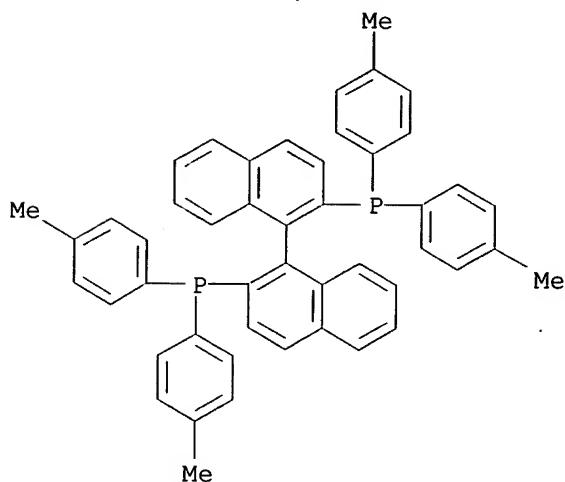
RN 76189-56-5 HCPLUS

CN Phosphine, (1S)-[1,1'-binaphthalene]-2,2'-diylbis[bis(4-methylphenyl)-  
 (9CI) (CA INDEX NAME)]



RN 100165-88-6 HCPLUS

CN Phosphine, (1S)-[1,1'-binaphthalene]-2,2'-diylbis[bis(4-methylphenyl)-  
 (9CI) (CA INDEX NAME)]



L34 ANSWER 17 OF 19 HCAPLUS COPYRIGHT 2003 ACS  
 AN 1996:440836 HCAPLUS  
 DN 125:168246  
 TI An Improved Procedure for the Resolution of (rac)-Ethylenebis(tetrahydroindenyl)Titanium Derivatives  
 AU Chin, Bain; Buchwald, Stephen L.  
 CS Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA, 02139, USA  
 SO Journal of Organic Chemistry (1996), 61(16), 5650-5651  
 CODEN: JOCEAH; ISSN: 0022-3263  
 PB American Chemical Society  
 DT Journal  
 LA English  
 CC 29-10 (Organometallic and Organometalloidal Compounds)  
 AB The resoln. of (rac)-ethylene-1,2-bis(.eta.5-4,5,6,7-tetrahydro-1-indenyl)titanium dichloride [(rac)-1] was effected with (R)-2,2'-binaphth-1-ol and p-aminobenzoic acid yielding (S,S)-1 and (R,R)-ethylene-1,2-bis(.eta.5-4,5,6,7-tetrahydro-1-indenyl)titanium (R)-1,1'-binaphth-2-olate. (S,S)-1 was demonstrated to be an effective precatalyst for asym. imine hydrogenation.  
 ST resoln ethylenebistetrahydroindenyltitanium dichloride; titanium ethylenebistetrahydroindenyl dichloride resoln; imine hydrogenation ethylenebistetrahydroindenyltitanium dichloride catalyst  
 IT Hydrogenation catalysts  
 (ethylenebistetrahydroindenyltitanium compds. for imines)  
 IT Resolution  
 (of ethylenebistetrahydroindenyltitanium dichloride)  
 IT 700-91-4  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (ethylenebistetrahydroindenyltitanium compds. as catalysts for hydrogenation of)  
 IT 1006-64-0P, 2-Phenylpyrrolidine  
 RL: SPN (Synthetic preparation); PREP (Preparation)  
 (ethylenebistetrahydroindenyltitanium compds. as catalysts in prepn. of)  
 IT 150-13-0, p-Aminobenzoic acid 18531-94-7  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (in resoln. of ethylenebistetrahydroindenyltitanium dichloride)  
 IT 180405-11-2P  
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)  
 (prep. and acidification of)

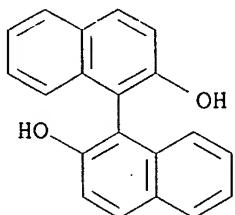
IT 83462-46-8P 143063-72-3P  
 RL: CAT (Catalyst use); PUR (Purification or recovery); SPN (Synthetic preparation); PREP (Preparation); USES (Uses)  
 (prepn. and hydrogenation catalyst for imines)

IT 83417-94-1  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (resoln. of)

IT 18531-94-7  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (in resoln. of ethylenebistetrahydroindenyltitanium dichloride)

RN 18531-94-7 HCPLUS

CN [1,1'-Binaphthalene]-2,2'-diol, (1R)- (9CI) (CA INDEX NAME)



L34 ANSWER 18 OF 19 HCPLUS COPYRIGHT 2003 ACS  
 AN 1996:418146 HCPLUS  
 DN 125:167030  
 TI An Improved Catalyst System for Aromatic Carbon-Nitrogen Bond Formation:  
 The Possible Involvement of Bis(Phosphine) Palladium Complexes as Key  
 Intermediates  
 AU Wolfe, John P.; Wagaw, Seble; Buchwald, Stephen L.  
 CS Department of Chemistry, Massachusetts Institute of Technology, Cambridge,  
 MA, 02139, USA  
 SO Journal of the American Chemical Society (1996), 118(30),  
 7215-7216  
 CODEN: JACSAT; ISSN: 0002-7863  
 PB American Chemical Society  
 DT Journal  
 LA English  
 CC 22-4 (Physical Organic Chemistry)  
 OS CASREACT 125:167030  
 AB The combination of Pd<sub>2</sub>(dba)<sub>3</sub> (dba=dibenzylideneacetone) and BINAP in the presence of NaOtBu constitutes a superior catalyst system for the cross coupling of amines with aryl bromides. Its success also suggests the viability of bis(phosphine)palladium intermediates in the key steps of the catalytic cycle. Two complexes, (BINAP)Pd(dba) and (BINAP)Pd(4-t-butylphenyl)(Br), were prep'd. and were found to be chem. and kinetically competent as intermediates in the catalytic sequence.  
 ST arylation amines palladium dba BINAP mechanism  
 IT Arylation  
 Arylation catalysts  
 (Pd<sub>2</sub>(dba)<sub>3</sub>/BINAP in presence of NaOtBu as catalyst for cross-coupling of amines with aryl bromides)  
 IT Aryl bromides  
 RL: PEP (Physical, engineering or chemical process); RCT (Reactant); PROC (Process); RACT (Reactant or reagent)  
 (Pd<sub>2</sub>(dba)<sub>3</sub>/BINAP in presence of NaOtBu as catalyst for cross-coupling of amines with aryl bromides)  
 IT Amines, reactions  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (Pd<sub>2</sub>(dba)<sub>3</sub>/BINAP in presence of NaOtBu as catalyst for cross-coupling of amines with aryl bromides)

IT Bond formation  
 (carbon-nitrogen, Pd<sub>2</sub>(dba)<sub>3</sub>/BINAP in presence of NaOtBu as catalyst for cross-coupling of amines with aryl bromides)

IT 98-06-6  
 RL: CAT (Catalyst use); FMU (Formation, unclassified); FORM (Formation, nonpreparative); USES (Uses)  
 (Pd complexes; Pd<sub>2</sub>(dba)<sub>3</sub>/BINAP in presence of NaOtBu as catalyst for cross-coupling of amines with aryl bromides)

IT 6163-58-2  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (Pd complexes; Pd<sub>2</sub>(dba)<sub>3</sub>/BINAP in presence of NaOtBu as catalyst for cross-coupling of amines with aryl bromides)

IT 51364-51-3, Tris(dibenzylideneacetone)dipalladium 98327-87-8, BINAP  
 RL: CAT (Catalyst use); USES (Uses)  
 (Pd<sub>2</sub>(dba)<sub>3</sub>/BINAP in presence of NaOtBu as catalyst for cross-coupling of amines with aryl bromides)

IT 553-94-6, 2-Bromo-p-xylene 556-96-7, 3,5-Dimethylphenyl bromide  
 578-57-4, 2-Bromoanisole 623-00-7, p-Bromobenzonitrile 698-00-0,  
 2-Bromo-N,N-dimethylaniline 17789-14-9, 2-(3-Bromophenyl)-1,3-dioxolane  
 27060-75-9, 4-Bromo-3-methylanisole 69038-74-0, tert-Butyl m-bromobenzoate  
 RL: PEP (Physical, engineering or chemical process); RCT (Reactant); PROC (Process); RACT (Reactant or reagent)  
 (Pd<sub>2</sub>(dba)<sub>3</sub>/BINAP in presence of NaOtBu as catalyst for cross-coupling of amines with aryl bromides)

IT 100-46-9, Benzylamine, reactions 100-61-8, N-Methylaniline, reactions  
 108-91-8, Cyclohexylamine, reactions 111-26-2, Hexylamine 2038-03-1,  
 N-(2-Aminoethyl)morpholine  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (Pd<sub>2</sub>(dba)<sub>3</sub>/BINAP in presence of NaOtBu as catalyst for cross-coupling of amines with aryl bromides)

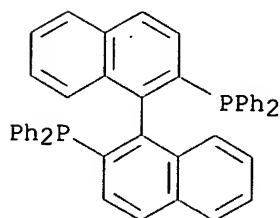
IT 109-01-3P, N-Methylpiperazine 13342-30-8P 54263-65-9P 124043-95-4P  
 180336-47-4P 180336-48-5P 180336-49-6P 180336-50-9P 180336-51-0P  
 180336-52-1P 180336-53-2P 180336-54-3P 180336-55-4P  
 RL: SPN (Synthetic preparation); PREP (Preparation)  
 (Pd<sub>2</sub>(dba)<sub>3</sub>/BINAP in presence of NaOtBu as catalyst for cross-coupling of amines with aryl bromides)

IT 538-58-9  
 RL: CAT (Catalyst use); FMU (Formation, unclassified); FORM (Formation, nonpreparative); USES (Uses)  
 (complex with Pd and binap; Pd<sub>2</sub>(dba)<sub>3</sub>/BINAP in presence of NaOtBu as catalyst for cross-coupling of amines with aryl bromides)

IT 98327-87-8, BINAP  
 RL: CAT (Catalyst use); USES (Uses)  
 (Pd<sub>2</sub>(dba)<sub>3</sub>/BINAP in presence of NaOtBu as catalyst for cross-coupling of amines with aryl bromides)

RN 98327-87-8 HCPLUS

CN Phosphine, [1,1'-binaphthalene]-2,2'-diylbis[diphenyl- (9CI) (CA INDEX NAME)]



L34 ANSWER 19 OF 19 HCAPLUS COPYRIGHT 2003 ACS  
 AN 1991:163623 HCAPLUS  
 DN 114:163623  
 TI Enantioselective, zirconium-mediated synthesis of allylic amines  
 AU Grossman, Robert B.; Davis, William M.; Buchwald, Stephen L.  
 CS Dep. Chem., Massachusetts Inst. Technol., Cambridge, MA, 02139, USA  
 SO Journal of the American Chemical Society (1991), 113(6), 2321-2  
 CODEN: JACSAT; ISSN: 0002-7863  
 DT Journal  
 LA English  
 CC 25-4 (Benzene, Its Derivatives, and Condensed Benzenoid Compounds)  
 Section cross-reference(s): 29  
 OS CASREACT 114:163623  
 AB The ethylene-1,2-bis(.eta.5-4,5,6,7-tetrahydro-1-indenyl)zirconium dichloride-mediated coupling reaction of a chiral N-arylamines with nonactivated alkynes gave enantiomerically pure allylic N-arylamines. The key step in the reaction sequence is the diastereoselective formation of an imine complex via C-H bond activation. Thus, N-pentylaniline was lithiated and added to (S,S)-ethylene-1,2-bis(.eta.5-4,5,6,7-tetrahydro-1-indenyl)zirconium dichloride trifluoromethanesulfonate and 2-butyne and the intermediate metallacycle complex was hydrolyzed to give 72% (2E,4S)-(+)-4-(phenylamino)-3-methyl-2-octene.  
 ST asym synthesis allyl arylamine; alkyne coupling arylamine ethylenebisindenylzirconium chloride; allyl arylamine asym synthesis; anilide coupling alkyne ethylenebisindenylzirconium chloride; arylamine coupling alkyne ethylenebisindenylzirconium chloride; coupling arylamine alkyne ethylenebisindenylzirconium chloride; ethylenebisindenylzirconium chloride coupling arylamine alkyne; pentylanilide coupling butyne ethyleneindenylzirconium chloride; phenylaminomethyl asym synthesis; octene phenylaminomethyl asym synthesis; zirconium ethylenebisindenyl coupling arylamine alkyne  
 IT Alkynes  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (coupling reaction of, with lithium anilides, chiral ethylenebis(tetrahydroindenyl)zirconium dichloride-catalyzed)  
 IT Asymmetric synthesis and induction  
 (of allylic N-arylamines, by coupling reaction of alkynes with lithium anilides, chiral ethylenebis(tetrahydroindenyl)zirconium dichloride-catalyzed)  
 IT Stereochemistry  
 (of coupling reaction of lithium anilides with alkynes, chiral ethylenebis(tetrahydroindenyl)zirconium dichloride-catalyzed)  
 IT Amines, reactions  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (aryl, lithiation and coupling reaction of, with alkynes, chiral ethylenebis(tetrahydroindenyl)zirconium dichloride-catalyzed)  
 IT Coupling reaction catalysts  
 (stereoselective, ethylenebis(tetrahydroindenyl)zirconium dichloride, for lithium anilides with alkynes)  
 IT Coupling reaction  
 (stereoselective, of alkynes with lithium anilides, chiral ethylenebis(tetrahydroindenyl)zirconium dichloride-catalyzed)  
 IT 20445-33-4, (S)-Methoxytrifluoromethylphenylacetyl chloride  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (esterification of, with (phenylamino)phenylbutanol)  
 IT 18531-99-2, (S)-1,1'-Binaphth-2,2'-diol  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (lithiation and reaction of, with ethylene bis[tetrahydroindenyl]zirconium dichloride)  
 IT 132802-28-9P  
 RL: SPN (Synthetic preparation); PREP (Preparation)  
 (prepn. and conversion of, to Mosher ester)  
 IT 132802-32-5P

IT 132802-21-2P, N-[6-(tert-Butyldimethylsilyl)oxy]-1-hexyl]aniline  
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)  
 (prepn. and lithiation and reaction of, with bis(tetrahydroindenyl)dimethylzirconium trifluoromethanesulfonate as chiral auxiliary and alkyne)

IT 132881-66-4P  
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)  
 (prepn. and methylation of)

IT 129368-70-3P, 1-Bromo-6-[(tert-butyldimethylsilyl)oxy]hexane  
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)  
 (prepn. and reaction of, with aniline)

IT 132881-67-5P  
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)  
 (prepn. and reaction of, with triflic acid, properties of, as chiral auxiliary for reaction of lithium anilides with alkynes)

IT 132802-13-2P 132802-14-3P 132802-15-4P 132802-16-5P 132802-17-6P  
 132802-18-7P 132802-19-8P 132802-20-1P 132802-22-3P 132802-23-4P  
 132802-24-5P 132802-25-6P 132802-26-7P 132802-27-8P 132802-29-0P  
 RL: SPN (Synthetic preparation); PREP (Preparation)  
 (prepn. of)

IT 103-32-2, N-Benzylaniline 103-69-5, N-Ethylaniline 104-48-3,  
 N-Ethyl-p-anisidine 588-47-6, N-Isobutylaniline  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (reaction of, with bis(tetrahydroindenyl)dimethylzirconium trifluoromethanesulfonate as chiral auxiliary and alkynes)

IT 123-38-6, Propionaldehyde, reactions 592-41-6, 1-Hexene, reactions  
 673-32-5, 1-Phenyl-1-propyne 6224-91-5, 1-(Trimethylsilyl)-1-propyne  
 110519-15-8  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (reaction of, with bis(tetrahydroindenyl)dimethylzirconium trifluoromethanesulfonate as chiral auxiliary and lithium anilide)

IT 18162-48-6, tert-Butyldimethylchlorosilane  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (reaction of, with bromohexanol)

IT 2655-27-8, N-Pentylaniline  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (reaction of, with chiral bis(tetrahydroindenyl)dimethylzirconium trifluoromethanesulfonate as chiral auxiliary and alkynes)

IT 503-17-3, 2-Butyne  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (reaction of, with chiral bis(tetrahydroindenyl)dimethylzirconium trifluoromethanesulfonate as chiral auxiliary and lithium anilides)

IT 100163-29-9  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (reaction of, with chiral lithium binaphthdiol)

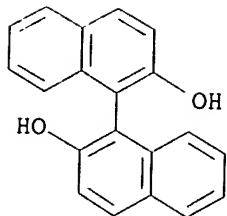
IT 132802-31-4  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (reaction of, with pentylaniline and butyne)

IT 4286-55-9, 6-Bromo-1-hexanol  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (silylation of, with butyldimethylchlorosilane)

IT 18531-99-2, (S)-1,1'-Binaphth-2,2'-diol  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (lithiation and reaction of, with ethylene bis[tetrahydroindenyl]zirconium dichloride)

RN 18531-99-2 HCPLUS

CN [1,1'-Binaphthalene]-2,2'-diol, (1S)- (9CI) (CA INDEX NAME)



=> d all hitstr tot 135

L35 ANSWER 1 OF 3 HCPLUS COPYRIGHT 2003 ACS  
 AN 1998:239186 HCPLUS  
 DN 128:282703  
 TI Preparation of aryl ethers  
 IN Buchwald, Stephen L.; Wolfe, John P.; Palucki, Michael  
 PA Massachusetts Institute of Technology, USA; Buchwald, Stephen L.; Wolfe, John P.; Palucki, Michael  
 SO PCT Int. Appl., 72 pp.  
 CODEN: PIXXD2  
 DT Patent  
 LA English  
 IC ICM. C07C043-20  
 ICS C07C041-16; C07C253-30; C07D307-79; C07D311-58; C07D313-08  
 CC 25-9 (Benzene, Its Derivatives, and Condensed Benzenoid Compounds)  
 FAN.CNT 1

|      | PATENT NO.  | KIND               | DATE         | APPLICATION NO. | DATE         |
|------|---|--------------------|--------------|-----------------|--------------|
| PI   | WO 9815515  | A1                 | 19980416     | WO 1997-US18719 | 19971010 <-- |
|      | W: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM |                    |              |                 |              |
|      | RW: GH, KE, LS, MW, SD, SZ, UG, ZW, AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG  |                    |              |                 |              |
|      | US 5847166  | A                  | 19981208     | US 1996-728449  | 19961010 <-- |
|      | AU 9747592  | A1                 | 19980505     | AU 1997-47592   | 19971010 <-- |
|      | EP 1027316  | A1                 | 20000816     | EP 1997-910139  | 19971010 <-- |
|      | R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, FI   |                    |              |                 |              |
|      | JP 2001501954   | T2                 | 20010213     | JP 1998-517804  | 19971010 <-- |
|      | EP 1245553  | A2                 | 20021002     | EP 2002-12164   | 19971010 <-- |
|      | R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, FI   |                    |              |                 |              |
|      | EP 1254884  | A2                 | 20021106     | EP 2002-12284   | 19971010 <-- |
|      | R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, FI   |                    |              |                 |              |
|      | US 6166226  | A                  | 20001226     | US 1998-206820  | 19981208 <-- |
|      | US 2001008942   | A1                 | 20010719     | US 2000-747280  | 20001221 <-- |
| PRAI | US 1996-728449  | A                  | 19961010 <-- |                 |              |
|      | EP 1997-910139  | A3                 | 19971010 <-- |                 |              |
|      | WO 1997-US18719   | W                  | 19971010 <-- |                 |              |
|      | US 1998-206820  | A1                 | 19981208 <-- |                 |              |
| OS   | CASREACT  | 128:282703; MARPAT | 128:282703   |                 |              |

AB The title process comprises reaction of an alc. with an arom. compd. ArX in the presence of a base and a transition metal catalyst comprising complexes of Pt, Pd, or Ni such that the activated substituent X conjugate acid HX has a pKa of <5.0. Thus, 2-BrC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>CMe<sub>2</sub>OH was maintained with Pd(OAc)<sub>2</sub> and tol-BINAP in PhMe contg. K<sub>2</sub>CO<sub>3</sub> at 100.degree. to give 89% 2,3-dihydro-2,2-dimethylbenzofuran. Kinetic data supporting mechanistic anal. of claimed reactions were given.

ST aryl ether prepn; alkoxylation aryl halide catalyst

IT Ethers, preparation

RL: IMF (Industrial manufacture); SPN (Synthetic preparation); PREP (Preparation)

(alkyl aryl; prepn. of aryl ethers)

IT Etherification catalysts

Etherification kinetics

(prepn. of aryl ethers)

IT 630-19-3P, Pivalaldehyde

RL: BYP (Byproduct); PREP (Preparation)

(prepn. of aryl ethers)

IT 193001-13-7P 193001-19-3P 193001-21-7P 193001-31-9P 193001-39-7P

RL: IMF (Industrial manufacture); RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)

(prepn. of aryl ethers)

IT 874-90-8P, 4-Methoxybenzonitrile 1198-96-5P, 3,4-Dihydro-2,2-dimethyl-2H-1-benzopyran 6337-33-3P, 2,2-Dimethyl-2,3-dihydrobenzofuran 13030-26-7P, 3,4-Dihydro-2-methyl-2H-1-benzopyran 21571-62-0P, 1-Cyclohexyloxynaphthalene 24432-40-4P 31603-95-9P 52805-36-4P, 4-Benzylxybenzonitrile 79615-68-2P, 4-(2,2-Dimethylpropoxy)benzonitrile 91949-95-0P, 4-Isopropoxybenzonitrile 124773-73-5P 183864-52-0P 183864-53-1P 183864-54-2P 183864-55-3P 183864-56-4P 183864-57-5P 185259-36-3P, 4-tert-Butoxybenzonitrile 188527-52-8P 188527-54-0P 188527-60-8P 188527-62-0P 188527-64-2P, 2-Chloro-4-cyclohexyloxybenzonitrile 188527-66-4P, 2-Chloro-4-(1-phenylethoxy)benzonitrile 188527-68-6P, 2-Chloro-4-tert-butoxybenzonitrile 188527-70-0P, 4-Bromo-2-cyclohexyloxybenzonitrile 188527-72-2P, 4-Bromo-2-(1-phenylethoxy)benzonitrile 205752-38-1P, 4-Cyclopentyloxybenzonitrile

RL: IMF (Industrial manufacture); SPN (Synthetic preparation); PREP (Preparation)

(prepn. of aryl ethers)

IT 67-63-0, 2-Propanol, reactions 90-11-9, 1-Bromonaphthalene 96-41-3, Cyclopentanol 98-85-1, 1-Phenylethanol 100-51-6, Benzyl alcohol, reactions 108-93-0, Cyclohexanol, reactions 402-43-7, 4-Bromobenzotrifluoride 584-02-1, 3-Pentanol 623-00-7, 4-Bromobenzonitrile 865-48-5, Sodium tert-butoxide 1564-64-3, 9-Bromoanthracene 2081-44-9 2216-51-5 3972-65-4, 4-tert-Butylbromobenzene 6163-58-2 12150-46-8 51364-51-3 55553-85-0, 1-Propanol, 2,2-Dimethyl-, potassium salt 67130-96-5, 2-Bromo-.alpha.-methylbenzenepropanol 99646-28-3 126495-44-1, 2-Bromo-.alpha.,.alpha.-dimethylbenzeneeethanol 142569-52-6 154607-01-9, 4-Bromo-2-chlorobenzonitrile 183864-38-2 183864-40-6 183864-42-8 183864-44-0 183864-45-1 183864-47-3, 2-Bromo-.alpha.,.alpha.-dimethylbenzenepropanol 183864-49-5 183864-50-8 183864-51-9

RL: RCT (Reactant); RACT (Reactant or reagent)

(prepn. of aryl ethers)

RE.CNT 2 THERE ARE 2 CITED REFERENCES AVAILABLE FOR THIS RECORD

RE

(1) Bates, R; JOURNAL OF ORGANIC CHEMISTRY 1982, V47(22), P4374 HCPLUS  
 (2) Cramer, R; JOURNAL OF ORGANIC CHEMISTRY 1975, V40(16), P2267 HCPLUS

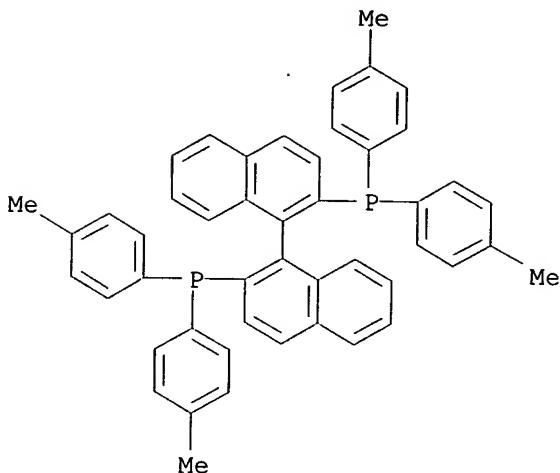
IT 99646-28-3

RL: RCT (Reactant); RACT (Reactant or reagent)

(prepn. of aryl ethers)

RN 99646-28-3 HCPLUS

CN Phosphine, (1R)-[1,1'-binaphthalene]-2,2'-diylbis[bis(4-methylphenyl)-  
(9CI) (CA INDEX NAME)]



L35 ANSWER 2 OF 3 HCAPLUS COPYRIGHT 2003 ACS  
 AN 1994:322918 HCAPLUS  
 DN 120:322918  
 TI Catalytic asymmetric and non-asymmetric reduction of imines and oximes using metal catalysts  
 IN Buchwald, Stephen L.; Willoughby, Christopher A.  
 PA Massachusetts Institute of Technology, USA  
 SO U.S., 10 pp. Cont.-in-part of U.S. Ser. No. 698,940, abandoned.  
 CODEN: USXXAM  
 DT Patent  
 LA English  
 IC ICM C07D207-02  
 ICS . C07D307-02; C07D207-06; C07C209-40; C07C209-52  
 NCL 548577000  
 CC 25-4 (Benzene, Its Derivatives, and Condensed Benzenoid Compounds)  
 Section cross-reference(s): 67  
 FAN.CNT 8

|      | PATENT NO.  | KIND | DATE         | APPLICATION NO. | DATE         |
|------|---|------|--------------|-----------------|--------------|
| PI   | US 5292893  | A    | 19940308     | US 1991-792229  | 19911114 <-- |
|      | US 5286878  | A    | 19940215     | US 1990-616892  | 19901121 <-- |
|      | CA 2096747  | AA   | 19920522     | CA 1991-2096747 | 19911121 <-- |
|      | WO 9209545  | A2   | 19920611     | WO 1991-US8738  | 19911121 <-- |
|      | WO 9209545  | A3   | 19921029     |                 |              |
|      | W: CA, JP   |      |              |                 |              |
|      | RW: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LU, NL, SE    |      |              |                 |              |
|      | EP 558656   | A1   | 19930908     | EP 1992-901632  | 19911121 <-- |
|      | EP 558656   | B1   | 19960417     |                 |              |
|      | R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE |      |              |                 |              |
|      | JP 06502867   | T2   | 19940331     | JP 1992-502333  | 19911121 <-- |
|      | AT 136878   | E    | 19960515     | AT 1992-901632  | 19911121 <-- |
|      | US 5442119  | A    | 19950815     | US 1993-90338   | 19930712 <-- |
|      | US 5489682  | A    | 19960206     | US 1994-195358  | 19940210 <-- |
| PRAI | US 1990-616892  |      | 19901121 <-- |                 |              |
|      | US 1991-698940  |      | 19910513 <-- |                 |              |
|      | US 1991-698939  |      | 19910513 <-- |                 |              |
|      | US 1991-749111  |      | 19910823 <-- |                 |              |
|      | US 1991-792227  |      | 19911114 <-- |                 |              |
|      | US 1991-792229  |      | 19911114 <-- |                 |              |

US 1991-792233            19911114 <--  
 WO 1991-US8738            19911121 <--  
 US 1993-90338            19930712 <--  
 OS CASREACT 120:322918; MARPAT 120:322918  
 AB The catalytic asym. redn. of imines [e.g., PhC(:NMe)Me], oximes, and hydrazones using chiral catalysts [e.g., (R,R)-ethylene-1,2-bis(.eta.5-4,5,6,7-tetrahydroindenyl)titanium (R)-1,1'-binaphth-2,2'diolate], to chiral amines (e.g., N-methyl-1-phenylethylamine) is described where the redn. is carried out in the presence of an inert gas or in a H atm., where H is the stoichiometric reducing agent (i.e., hydrogenation).  
 ST asym redn oxime; imine asym redn prepn amine; catalyst chiral asym hydrogenation imine  
 IT Imines  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (asym. redn. or hydrogenation of, amines from)  
 IT Oximes  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (asym. redn. or hydrogenation of, to chiral amines, chiral catalysts for)  
 IT Siloxanes and Silicones, uses  
 RL: CAT (Catalyst use); USES (Uses)  
 (catalysts, contg. chiral transition metal complexes, for asym. hydrogenation or redn. of imines or oximes to chiral amines)  
 IT Amines, preparation  
 RL: SPN (Synthetic preparation); PREP (Preparation)  
 (chiral, prepn. of, by asym. redn. or hydrogenation of imines or oximes in presence of chiral catalysts)  
 IT Hydrogenation catalysts  
 Reduction catalysts  
 (stereoselective, chiral transition metal complexes, for conversion of imines and oximes to chiral amines)  
 IT Hydrogenation  
 Reduction  
 (stereoselective, of oximes and imines to chiral amines)  
 IT 700-91-4  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (asym. hydrogenation of, catalyst for)  
 IT 6907-71-7, Acetophenone N-methylimine 14428-98-9, Acetophenone N-benzylimine 63459-02-9 143417-07-6 143417-08-7  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (asym. redn. of, catalyst for)  
 IT 546-68-9, Titanium tetrakisopropoxide 992-92-7, Titanium tetramethoxide 1271-19-8, Titanocene dichloride 3087-36-3, Titanium tetraethoxide 3087-37-4, Titanium tetrapropoxide 3981-83-7, Trichlorotitanium isopropoxide 5593-70-4, Titanium tetrabutoxide 60955-54-6, Titanocene monochloride  
 RL: CAT (Catalyst use); USES (Uses)  
 (catalyst, contg. chiral ligands, for asym. hydrogenation or redn. of oximes or imines to chiral amines)  
 IT 542-91-6, Diethylsilane 693-25-4, n-Pentylmagnesium bromide 775-12-2, Diphenylsilane 998-30-1, Triethoxysilane 1066-26-8, Sodium acetylidyde 1111-74-6, Dimethylsilane 2487-90-3, Trimethoxysilane 7803-62-5, Silane, uses 22722-98-1, Sodium bis(2-methoxyethoxy)aluminum hydride  
 RL: CAT (Catalyst use); USES (Uses)  
 (catalyst, contg. transition metals, for asym. hydrogenation or redn. of oximes or imines to chiral amines)  
 IT 109-72-8, Butyl lithium, uses 694-53-1, Phenylsilane 83417-93-0 143063-72-3  
 RL: CAT (Catalyst use); USES (Uses)  
 (catalyst, for asym. hydrogenation or redn. of oximes or imines to chiral amines)  
 IT 299-42-3 321-98-2 18531-94-7 18531-99-2 20439-47-8  
 21436-03-3 93379-49-8

RL: RCT (Reactant); RACT (Reactant or reagent)  
 (catalysts contg. transition metals, for asym. hydrogenation or redn.  
 of imines or oximes to chiral amines)

IT 1333-74-0  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (hydrogenation, stereoselective, of oximes and imines to chiral amines)

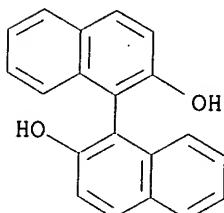
IT 38235-77-7P  
 RL: SPN (Synthetic preparation); PREP (Preparation)  
 (prepn. of, catalyst for)

IT 1006-64-0P 2084-72-2P 32512-24-6P 61806-77-7P 143063-65-4P  
 RL: SPN (Synthetic preparation); PREP (Preparation)  
 (prepn. of, enantioselective, catalyst for)

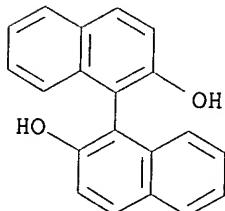
IT 18531-94-7 18531-99-2  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (catalysts contg. transition metals, for asym. hydrogenation or redn.  
 of imines or oximes to chiral amines)

RN 18531-94-7 HCPLUS

CN [1,1'-Binaphthalene]-2,2'-diol, (1R)- (9CI) (CA INDEX NAME)



RN 18531-99-2 HCPLUS  
 CN [1,1'-Binaphthalene]-2,2'-diol, (1S)- (9CI) (CA INDEX NAME)



L35 ANSWER 3 OF 3 HCPLUS COPYRIGHT 2003 ACS  
 AN 1994:134036 HCPLUS  
 DN 120:134036  
 TI Catalytic asymmetric reduction of acetophenone using metal catalysts  
 IN Buchwald, Stephen L.; Gutierrez, Alberto; Grossman, Robert B.  
 PA Massachusetts Institute of Technology, USA  
 SO U.S., 5 pp. Cont.-in-part of U.S. Ser. No. 698,939, abandoned.  
 CODEN: USXXAM  
 DT Patent  
 LA English  
 IC ICM C07C029-36  
 ICS C07C029-50  
 NCL 568814000  
 CC 25-16 (Benzene, Its Derivatives, and Condensed Benzenoid Compounds)  
 FAN.CNT 8

| PATENT NO.    | KIND | DATE     | APPLICATION NO. | DATE         |
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| PI US 5227538 | A    | 19930713 | US 1991-792227  | 19911114 <-- |

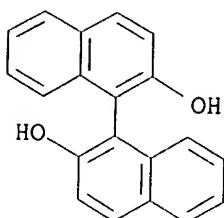
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     W: CA, JP  
     RW: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LU, NL, SE  
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 EP 558656 B1 19960417  
     R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE  
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 AT 136878 E 19960515 AT 1992-901632 19911121 <--  
 PRAI US 1990-616892 19901121 <--  
 US 1991-698939 19910513 <--  
 US 1991-698940 19910513 <--  
 US 1991-749111 19910823 <--  
 US 1991-792227 19911114 <--  
 US 1991-792229 19911114 <--  
 US 1991-792233 19911114 <--  
 WO 1991-US8738 19911121 <--  
 AB A process for the catalytic redn. of the title compd. (I) and in general ketones comprises (i) catalyst M(L)(L')(L''), etc., wherein M = group 3,4,5,6 metal, lanthanide, actinide, L,L',L'' = combination of H, alkyl, aryl, silyl, halo, RO, RS, R'RN wherein R, R' = H, alkyl, aryl; (ii) a stoichiometric amt. of a silane able to supply a hydride ion during the redn. reaction and (iii) a chiral additive such as amine, alc. org. acid, thil and phosphine, reacting a ketone substrate in presence of the mixt., and recovering and purifying the alc. product enriched in one enantiomer. A mixt. of Ti(IV) isopropoxide and triethoxysilane in THF was warmed to 46.degree., (R,R)-1,2-bis(benzylamino)cyclohexane was added followed by I to give MeCHPhOH with an ee of 37% of S enantiomer.  
 ST acetophenone asym redn catalyst phenylethanol  
 IT Siloxanes and Silicones, uses  
     RL: USES (Uses)  
         (polymethylhydro, reducing agents, for ketones)  
 IT Ketones, reactions  
     RL: RCT (Reactant); RACT (Reactant or reagent)  
         (redn. of, catalytic)  
 IT Reduction  
     (stereoselective, of ketones)  
 IT Reduction catalysts  
     (stereoselective, titanium alkoxide, for ketones)  
 IT 98-86-2, Acetophenone, reactions  
     RL: RCT (Reactant); RACT (Reactant or reagent)  
         (asym. redn. of, catalysts for)  
 IT 546-68-9, Titanium(IV) isopropoxide  
     RL: CAT (Catalyst use); USES (Uses)  
         (catalysts contg., for asym. redn. of acetophenol)  
 IT 992-92-7, Titanium (IV) methoxide 3087-36-3, Titanium (IV) ethoxide 3981-83-7, Trichlorotitanium (IV) isopropoxide 5593-70-4, Titanium (IV) butoxide  
     RL: CAT (Catalyst use); USES (Uses)  
         (catalysts, for asym. redn. of ketones)  
 IT 93379-48-7 143443-23-6, (R,R)-1,2-Bis(Benzylamino)cyclohexane  
     RL: RCT (Reactant); RACT (Reactant or reagent)  
         (chirable additive, in redn. of acetophenone)  
 IT 299-42-3 321-98-2 18531-94-7 18531-99-2,  
     (S)-1,1'-Bi-2-naphthol 20439-47-8, (1R,2R)-Diaminocyclohexane 21436-03-3, (1S,2S)-Diaminocyclohexane  
     RL: RCT (Reactant); RACT (Reactant or reagent)  
         (chiral additive, and redn. of ketones)  
 IT 98-85-1P, 1-Phenylethanol  
     RL: SPN (Synthetic preparation); PREP (Preparation)  
         (prepn. of, by catalytic asym. redn. of acetophenone)

IT 998-30-1, Triethoxysilane  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (reducing agent, for acetophenone)

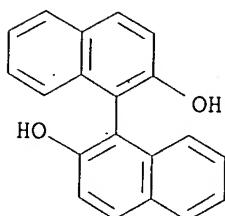
IT 18531-94-7 18531-99-2, (S)-1,1'-Bi-2-naphthol  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (chiral additive, and redn. of ketones)

RN 18531-94-7 HCPLUS

CN [1,1'-Binaphthalene]-2,2'-diol, (1R)- (9CI) (CA INDEX NAME)



RN 18531-99-2 HCPLUS  
 CN [1,1'-Binaphthalene]-2,2'-diol, (1S)- (9CI) (CA INDEX NAME)



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STRUCTURE FILE UPDATES: 11 MAY 2003 HIGHEST RN 514167-89-6  
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TSCA INFORMATION NOW CURRENT THROUGH JANUARY 6, 2003

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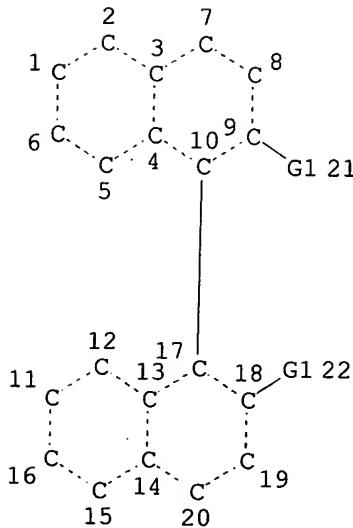
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Experimental and calculated property data are now available. See HELP PROPERTIES for more information. See STNote 27, Searching Properties in the CAS Registry File, for complete details:  
<http://www.cas.org/ONLINE/STN/STNOTES/stnotes27.pdf>

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L11 3 SEA FILE=REGISTRY ABB=ON PLU=ON L10 AND C34H40NP  
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Subsets for

Claim 10

X 7 4

VAR G1=N/P/AS/O/S

NODE ATTRIBUTES:

DEFAULT MLEVEL IS ATOM

DEFAULT ECLEVEL IS LIMITED

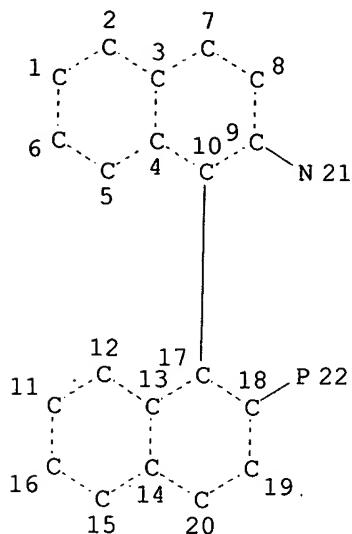
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NUMBER OF NODES IS 22

STEREO ATTRIBUTES: NONE

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 L46        STR



NODE ATTRIBUTES:

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 DEFAULT ECLEVEL IS LIMITED

GRAPH ATTRIBUTES:

RING(S) ARE ISOLATED OR EMBEDDED  
 NUMBER OF NODES IS 22

STEREO ATTRIBUTES: NONE

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100.0% PROCESSED      84 ITERATIONS  
 SEARCH TIME: 00.00.01

75 ANSWERS

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(FILE 'REGISTRY' ENTERED AT 09:36:26 ON 12 MAY 2003)  
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FILE 'HCAPLUS' ENTERED AT 09:39:41 ON 12 MAY 2003  
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 L50        7 S L49 AND (PY<=1998 OR PRY<=1998 OR AY<=1998)  
 L51        5 S L50 NOT L29-L34  
 L52        2 S L51 AND (PD<=19980710 OR PRD<=19980710 OR AD<=19980710)

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FILE LAST UPDATED: 11 May 2003 (20030511/ED)

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L52 ANSWER 1 OF 2 HCPLUS COPYRIGHT 2003 ACS  
AN 1998:787294 HCPLUS  
DN 130:124873  
TI Synthesis of 2-amino-2'-diphenylphosphino-1,1'-binaphthyl (MAP) and its accelerating effect on the Pd(0)-catalyzed N-arylation  
AU Vyskocil, Stepan; Smrcina, Martin; Kocovsky, Pavel  
CS Department of Organic Chemistry, Charles University, Prague, 128 40, Czech Rep.  
SO Tetrahedron Letters (1998), 39(50), 9289-9292  
CODEN: TELEAY; ISSN: 0040-4039  
PB Elsevier Science Ltd.  
DT Journal  
LA English  
CC 25-24 (Benzene, Its Derivatives, and Condensed Benzenoid Compounds)  
OS CASREACT 130:124873  
AB The title compd., synthesized in four steps from NOBIN, shows a dramatic accelerating effect on the Pd(0)-catalyzed Hartwig-Buchwald N-phenylation of 2'-amino-2-hydroxy-1,1'-binaphthalene and the corresponding diamine with PhBr. Partial kinetic resoln. was obsd. for the phenylation of the racemic amino alc. or diamine in presence of (S)-BINAP.  
ST aminodiphenylphosphinobinaphthalene prepn Hartwig Buchwald phenylation catalyst; binaphthylamine phenylation catalyst  
IT Arylation  
Arylation catalysts  
(Hartwig-Buchwald; prepn. of 2-amino-2'-diphenylphosphino-1,1'-binaphthyl and its accelerating effect on the Pd(0)-catalyzed N-arylation)  
IT 76189-56-5 98327-87-8  
RL: CAT (Catalyst use); USES (Uses)  
(prep. of 2-amino-2'-diphenylphosphino-1,1'-binaphthyl and its accelerating effect on the Pd(0)-catalyzed N-arylation)  
IT 216368-93-3P  
RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation); USES (Uses)  
(prep. of 2-amino-2'-diphenylphosphino-1,1'-binaphthyl and its accelerating effect on the Pd(0)-catalyzed N-arylation)  
IT 108-86-1, Bromobenzene, reactions 4488-22-6, [1,1'-Binaphthalene]-2,2'-diamine 4559-70-0, Diphenylphosphine oxide 18741-85-0 134532-03-9 137848-28-3  
RL: RCT (Reactant); RACT (Reactant or reagent)  
(prep. of 2-amino-2'-diphenylphosphino-1,1'-binaphthyl and its accelerating effect on the Pd(0)-catalyzed N-arylation)  
IT 216320-44-4P 216368-90-0P 216368-92-2P  
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT

(Reactant or reagent)

(prepn. of 2-amino-2'-diphenylphosphino-1,1'-binaphthyl and its accelerating effect on the Pd(0)-catalyzed N-arylation)

IT 17704-02-8P 210094-86-3P 210235-21-5P 216320-20-6P 219820-75-4P  
219820-80-1P

RL: SPN (Synthetic preparation); PREP (Preparation)

(prepn. of 2-amino-2'-diphenylphosphino-1,1'-binaphthyl and its accelerating effect on the Pd(0)-catalyzed N-arylation)

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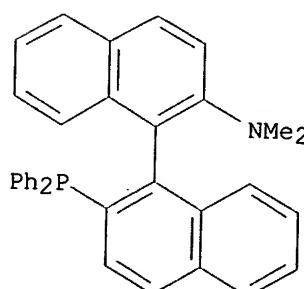
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IT 216368-93-3P

RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation);  
USES (Uses)

(prepn. of 2-amino-2'-diphenylphosphino-1,1'-binaphthyl and its accelerating effect on the Pd(0)-catalyzed N-arylation)

RN 216368-93-3 HCPLUS

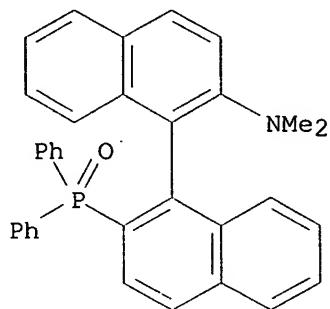
CN [1,1'-Binaphthalen]-2-amine, 2'-(diphenylphosphino)-N,N-dimethyl-, (1R)-  
(9CI) (CA INDEX NAME)

IT 216368-92-2P

RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)  
 (prepn. of 2-amino-2'-diphenylphosphino-1,1'-binaphthyl and its accelerating effect on the Pd(0)-catalyzed N-arylation)

RN 216368-92-2 HCPLUS

CN [1,1'-Binaphthalen]-2-amine, 2'-(diphenylphosphinyl)-N,N-dimethyl-, (1R)- (9CI) (CA INDEX NAME)



L52 ANSWER 2 OF 2 HCPLUS COPYRIGHT 2003 ACS

AN 1998:659145 HCPLUS

DN 130:24844

TI Derivatives of 2-Amino-2'-diphenylphosphino-1,1'-binaphthyl (MAP) and Their Application in Asymmetric Palladium(0)-Catalyzed Allylic Substitution

AU Vyskocil, Stepan; Smrcina, Martin; Hanus, Vladimir; Polasek, Miroslav; Kocovsky, Pavel

CS Department of Organic Chemistry, Department of Organic Chemistry Charles University, Prague, Czech Rep.

SO Journal of Organic Chemistry (1998), 63(22), 7738-7748  
CODEN: JOCEAH; ISSN: 0022-3263

PB American Chemical Society

DT Journal

LA English

CC 25-24 (Benzene, Its Derivatives, and Condensed Benzenoid Compounds)

OS CASREACT 130:24844

AB (R)-(+)-2-Amino-2'-hydroxy-1,1'-binaphthyl (NOBIN) can be readily converted into a series of novel N,N-disubstituted amino phosphines. The N,N-di-Me deriv. (MAP) was prep'd. via a sequence involving reductive alkylation with CH<sub>2</sub>O and NaBH<sub>4</sub>, Pd(0)-catalyzed coupling of the corresponding triflate with Ph<sub>2</sub>P(O)H, and redn. of the resulting phosphine oxide with Cl<sub>3</sub>SiH. Variation of this scheme was required for the prepn. of other N,N-disubstituted amino phosphines as the phosphinylation failed in the presence of bulky N substituents; the N-protected triflate was first coupled with Ph<sub>2</sub>P(O)H, and the resulting phosphine oxide was reduced with Cl<sub>3</sub>SiH to give the amino phosphine, which was then subjected to reductive alkylation with individual ketones and NaBH<sub>4</sub>. The new P,N-binaphthyls thus obtained (23-25 and 9) were utilized as chiral ligands in Pd(0)-catalyzed allylic substitution. The enantioselectivities obtained for racemic 1,3-diphenylprop-2-en-1-yl acetate and malonate nucleophiles are interpreted in terms of a chelated transition state and preferential attack at the allylic terminus that is trans with respect to the phosphorus acceptor atom.

ST aminodiphenylphosphinobinaphthyl prep'n stereoselective allylic substitution catalyst

IT Substitution reaction catalysts  
 (stereoselective; prep'n. of 2-amino-2'-diphenylphosphino-1,1'-

binaphthyl derivs. as auxiliaries in asym. palladium(0)-catalyzed allylic substitution)

IT 87802-78-6P 87802-79-7P 216369-05-0P  
 RL: BYP (Byproduct); PREP (Preparation)  
 (prepn. of 2-amino-2'-diphenylphosphino-1,1'-binaphthyl derivs. as auxiliaries in asym. palladium(0)-catalyzed allylic substitution)

IT 216368-93-3P 216369-08-3P 216369-09-4P  
 216369-10-7P  
 RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation);  
 USES (Uses)  
 (prepn. of 2-amino-2'-diphenylphosphino-1,1'-binaphthyl derivs. as auxiliaries in asym. palladium(0)-catalyzed allylic substitution)

IT 108-59-8, Dimethyl malonate 609-02-9, Dimethyl methylmalonate  
 7217-71-2 21040-45-9, (E)-Cinnamyl acetate 60187-67-9 85217-71-6  
 87751-69-7 121440-72-0 137848-28-3 216319-82-3 216319-84-5  
 216320-44-4 216368-94-4  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (prepn. of 2-amino-2'-diphenylphosphino-1,1'-binaphthyl derivs. as auxiliaries in asym. palladium(0)-catalyzed allylic substitution)

IT 216368-90-0P 216368-92-2P 216369-01-6P 216369-02-7P  
 216369-03-8P 216369-04-9P 216369-06-1P  
 216369-07-2P  
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)  
 (prepn. of 2-amino-2'-diphenylphosphino-1,1'-binaphthyl derivs. as auxiliaries in asym. palladium(0)-catalyzed allylic substitution)

IT 96482-63-2P 96482-64-3P 119793-72-5P 136656-89-8P 189884-53-5P  
 216075-90-0P 216319-83-4P 216368-97-7P 216369-00-5P  
 RL: SPN (Synthetic preparation); PREP (Preparation)  
 (prepn. of 2-amino-2'-diphenylphosphino-1,1'-binaphthyl derivs. as auxiliaries in asym. palladium(0)-catalyzed allylic substitution)

RE.CNT 203 THERE ARE 203 CITED REFERENCES AVAILABLE FOR THIS RECORD  
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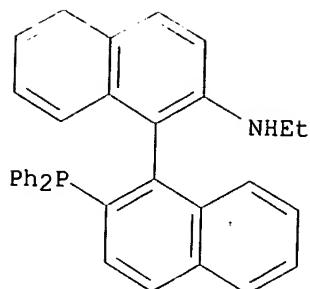
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IT 216369-05-0P

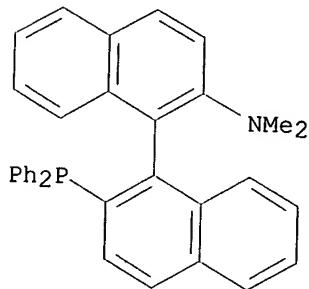
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 (prepn. of 2-amino-2'-diphenylphosphino-1,1'-binaphthyl derivs. as  
 auxiliaries in asym. palladium(0)-catalyzed allylic substitution)

RN 216369-05-0 HCPLUS

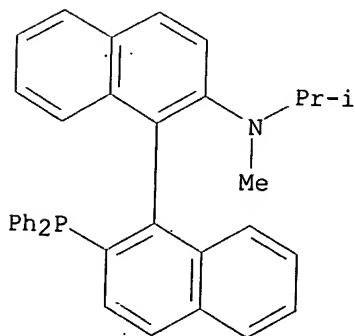
CN [1,1'-Binaphthalen]-2-amine, 2'-(diphenylphosphino)-N-ethyl-, (1R)- (9CI)  
 (CA INDEX NAME)



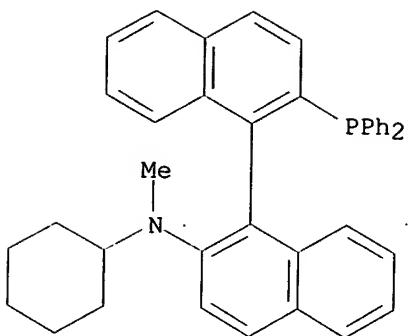
IT 216368-93-3P 216369-08-3P 216369-09-4P  
 RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation);  
 USES (Uses)  
 (prepn. of 2-amino-2'-(diphenylphosphino)-1,1'-binaphthyl derivs. as  
 auxiliaries in asym. palladium(0)-catalyzed allylic substitution)  
 RN 216368-93-3 HCPLUS  
 CN [1,1'-Binaphthalen]-2-amine, 2'-(diphenylphosphino)-N,N-dimethyl-, (1R)-  
 (9CI) (CA INDEX NAME)



RN 216369-08-3 HCPLUS  
 CN [1,1'-Binaphthalen]-2-amine, 2'-(diphenylphosphino)-N-methyl-N-(1-  
 methylethyl)-, (1R)- (9CI) (CA INDEX NAME)



RN 216369-09-4 HCPLUS  
 CN [1,1'-Binaphthalen]-2-amine, N-cyclohexyl-2'-(diphenylphosphino)-N-methyl-  
 , (1R)- (9CI) (CA INDEX NAME)



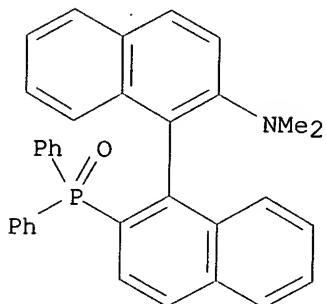
IT 216368-92-2P 216369-03-8P 216369-04-9P  
216369-06-1P 216369-07-2P

RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)

(prep. of 2-amino-2'-diphenylphosphino-1,1'-binaphthyl derivs. as auxiliaries in asym. palladium(0)-catalyzed allylic substitution)

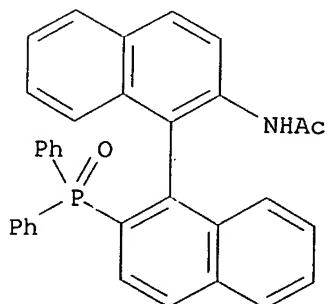
RN 216368-92-2 HCAPLUS

CN [1,1'-Binaphthalen]-2-amine, 2'-(diphenylphosphinyl)-N,N-dimethyl-, (1R)- (9CI) (CA INDEX NAME)



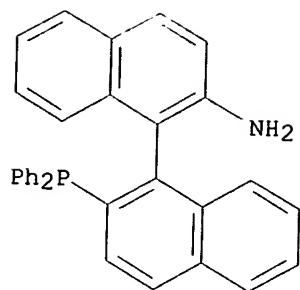
RN 216369-03-8 HCAPLUS

CN Acetamide, N-[ $(1R)$ -2'-(diphenylphosphinyl)[1,1'-binaphthalen]-2-yl]- (9CI) (CA INDEX NAME)



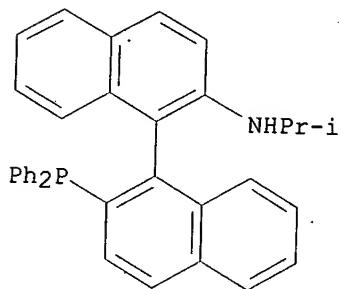
RN 216369-04-9 HCAPLUS

CN [1,1'-Binaphthalen]-2-amine, 2'-(diphenylphosphino)-, (1R)- (9CI) (CA INDEX NAME)



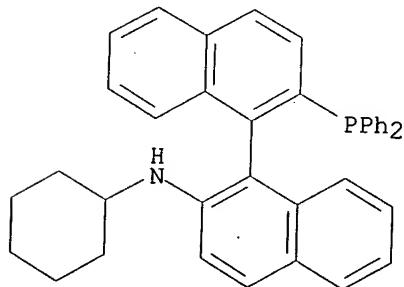
RN 216369-06-1 HCPLUS

CN [1,1'-Binaphthalen]-2-amine, 2'-(diphenylphosphino)-N-(1-methylethyl)-, (1R)- (9CI) (CA INDEX NAME)



RN 216369-07-2 HCPLUS

CN [1,1'-Binaphthalen]-2-amine, N-cyclohexyl-2'-(diphenylphosphino)-, (1R)- (9CI) (CA INDEX NAME)



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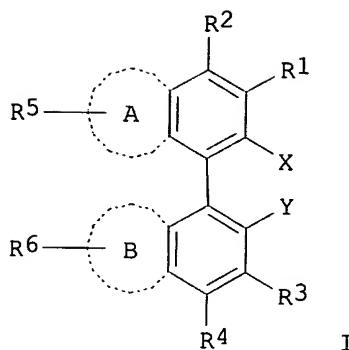
This file contains CAS Registry Numbers for easy and accurate substance identification.

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L81 ANSWER 1 OF 18 HCAPLUS COPYRIGHT 2003 ACS  
AN 2000:53646 HCAPLUS  
DN 132:108101  
TI Biaryl phosphine and amine ligands for improved transition metal-catalyzed processes  
IN Buchwald, Stephen; Old, David W.; Wolfe, John P.; Palucki, Michael; Kamikawa, Ken; Chieffi, Andrew; Sadighi, Joseph P.; Singer, Robert A.; Ahman, Jens  
PA Massachusetts Institute of Technology, USA  
SO PCT Int. Appl., 397 pp.  
CODEN: PIXXD2  
DT Patent  
LA English  
IC ICM C07F009-02  
CC 29-7 (Organometallic and Organometalloidal Compounds)  
Section cross-reference(s): 25  
FAN.CNT 2

|      | PATENT NO.   | KIND | DATE         | APPLICATION NO. | DATE         |
|------|--|------|--------------|-----------------|--------------|
| PI   | WO 2000002887  | A2   | 20000120     | WO 1999-US15450 | 19990709 <-- |
|      | WO 2000002887  | A3   | 20000629     |                 |              |
|      | W: CA, JP  |      |              |                 |              |
|      | RW: AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE |      |              |                 |              |
|      | US 6395916   | B1   | 20020528     | US 1998-113478  | 19980710 <-- |
|      | US 6307087   | B1   | 20011023     | US 1999-231315  | 19990113 <-- |
|      | CA 2336691   | AA   | 20000120     | CA 1999-2336691 | 19990709 <-- |
|      | EP 1097158   | A2   | 20010509     | EP 1999-933785  | 19990709 <-- |
|      | R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, FI  |      |              |                 |              |
|      | JP 2002520328  | T2   | 20020709     | JP 2000-559117  | 19990709 <-- |
| PRAI | US 1998-113478   | A    | 19980710 <-- |                 |              |
|      | US 1998-196855   | A    | 19981120     |                 |              |
|      | US 1999-231315   | A    | 19990113     |                 |              |
|      | US 1999-239024   | A    | 19990127     |                 |              |
|      | WO 1999-US15450  | W    | 19990709     |                 |              |
| OS   | MARPAT 132:108101  |      |              |                 |              |

GI



**AB** The present invention relates to the prepn. of novel biaryl phosphine and amine ligands (I) [wherein A and B = independently fused monocyclic or polycyclic cycloalkyl, cycloalkenyl, aryl, or heterocyclic rings of 4-8 atoms; X = NR<sub>2</sub>, PR<sub>2</sub>, AsR<sub>2</sub>, OR, or SR; Y = NR<sub>2</sub>, PR<sub>2</sub>, AsR<sub>2</sub>, OR, SR, SiR<sub>3</sub>, alkyl, or H; R-R<sub>6</sub> = independently H, halogen, (hetero)alkyl, alkenyl, alkynyl, hydroxy, alkoxy, silyloxy, amino, nitro, sulfhydryl, amide, carbonyl, ketone, anhydride, silyl, thioalkyl, ketone, ester, nitrile, (hetero)aryl, etc.] for transition metals and their use in metal-catalyzed carbon-heteroatom and carbon-carbon bond-forming reactions. Unexpected improvements over the prior art were demonstrated in transition metal-catalyzed aryl amination reactions, Suzuki couplings giving both biaryl and alkylaryl products, arylations and vinylations at the position .alpha. to carbonyl groups, and carbon-oxygen bond formation. The ligands and methods of the invention enable transformations utilizing aryl chlorides and bromides at room temp. at synthetically useful rates with extremely small amts. of catalyst relative to the limiting reagent. For example, coupling of p-chlorobenzonitrile and morpholine was catalyzed by 2.5 mol% Pd<sub>2</sub>(dba)<sub>3</sub>, 7.5 mol% of 2-(N,N-dimethylamino)-2'-(dicyclohexylphosphino)biphenyl, and NaOBu-t in DME at room temp. to provide 4-(4-morpholinyl)benzonitrile in 96% yield. Thus, the subject processes provide improvements in many features of the transition metal-catalyzed reactions, including the range of suitable substrates, reaction conditions, and efficiency.

**ST** biaryl phosphine ammine ligand prepn transition metal catalyst; amination aryl chloride bromide palladium catalysts; Suzuki coupling aryl chloride bromide palladium catalysts; ketone arylation vinylation palladium catalysts; etherification palladium catalysts

**IT** Amines, preparation  
RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation); USES (Uses)  
(arom.; prepn. of biaryl phosphine and amine ligands for improved palladium-catalyzed amination reactions, Suzuki couplings, arylations, vinylations, and carbon-oxygen bond formation reactions)

**IT** Ethers, preparation  
Ketones, preparation  
RL: SPN (Synthetic preparation); PREP (Preparation)  
(arom.; prepn. of biaryl phosphine and amine ligands for improved palladium-catalyzed amination reactions, Suzuki couplings, arylations, vinylations, and carbon-oxygen bond formation reactions)

**IT** Aryl halides  
Aryl halides  
RL: RCT (Reactant); RACT (Reactant or reagent)

(aryl chlorides; prepn. of biaryl phosphine and amine ligands for improved palladium-catalyzed amination reactions, Suzuki couplings, arylations, vinylations, and carbon-oxygen bond formation reactions)

IT Chlorides, reactions  
Chlorides, reactions  
RL: RCT (Reactant); RACT (Reactant or reagent)  
(aryl; prepn. of biaryl phosphine and amine ligands for improved palladium-catalyzed amination reactions, Suzuki couplings, arylations, vinylations, and carbon-oxygen bond formation reactions)

IT Transition metal complexes  
Transition metal complexes  
RL: CAT (Catalyst use); USES (Uses)  
(phosphine; prepn. of biaryl phosphine and amine ligands for improved palladium-catalyzed amination reactions, Suzuki couplings, arylations, vinylations, and carbon-oxygen bond formation reactions)

IT Amination  
Amination catalysts  
Arylation  
Arylation catalysts  
Cross-coupling reaction catalysts  
Etherification  
Etherification catalysts  
Suzuki coupling reaction  
Vinylation  
Vinylation catalysts  
(prepn. of biaryl phosphine and amine ligands for improved palladium-catalyzed amination reactions, Suzuki couplings, arylations, vinylations, and carbon-oxygen bond formation reactions)

IT Phosphines  
RL: CAT (Catalyst use); USES (Uses)  
(prepn. of biaryl phosphine and amine ligands for improved palladium-catalyzed amination reactions, Suzuki couplings, arylations, vinylations, and carbon-oxygen bond formation reactions)

IT Biaryls  
RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation); USES (Uses)  
(prepn. of biaryl phosphine and amine ligands for improved palladium-catalyzed amination reactions, Suzuki couplings, arylations, vinylations, and carbon-oxygen bond formation reactions)

IT Aryl bromides  
RL: RCT (Reactant); RACT (Reactant or reagent)  
(prepn. of biaryl phosphine and amine ligands for improved palladium-catalyzed amination reactions, Suzuki couplings, arylations, vinylations, and carbon-oxygen bond formation reactions)

IT Phosphines  
Phosphines  
RL: CAT (Catalyst use); USES (Uses)  
(transition metal complexes; prepn. of biaryl phosphine and amine ligands for improved palladium-catalyzed amination reactions, Suzuki couplings, arylations, vinylations, and carbon-oxygen bond formation reactions)

IT 534-17-8, Dicesium carbonate 3375-31-3, Diacetatopalladium 6476-37-5, Dicyclohexylphenylphosphine 14221-01-3, Tetrakis(triphenylphosphine)palladium 31570-04-4 51364-51-3, Tris(dibenzylideneacetone)dipalladium 54000-83-8, 2,6-Dimethoxyphenyl-di-t-butylphosphine 71042-54-1 74286-11-6 76189-56-5 91548-08-2 100165-88-6 133545-16-1 136779-28-7 139139-92-7 **145964-33-6** 149341-34-4 155806-35-2 213774-71-1 224311-49-3 247940-06-3 255837-14-0, 2,4,6-Trimethoxyphenyl-di-t-butylphosphine 255837-17-3 255837-19-5 255882-15-6 255882-16-7 255882-17-8 255882-18-9  
RL: CAT (Catalyst use); USES (Uses)  
(catalyst; prepn. of biaryl phosphine and amine ligands for improved palladium-catalyzed amination reactions, Suzuki couplings, arylations,

vinylations, and carbon-oxygen bond formation reactions)

IT 698-00-0P 4688-76-0P 18937-92-3P 20837-12-1P, 2-Bromo-2'-methoxy-  
1,1'-biphenyl 59734-92-8P 75295-57-7P 89291-23-6P 89787-12-2P,  
2-Isopropylphenylboronic acid 128796-39-4P, 4-  
(Trifluoromethyl)phenylboronic acid 224311-57-3P 224311-58-4P  
224311-59-5P 251320-87-3P, 2-Bromo-2'-methylbiphenyl 251320-89-5P,  
2-Bromo-2'-isopropylbiphenyl 255837-15-1P, 2-Bromo-4'-  
(trifluoromethyl)biphenyl 255837-16-2P 255837-18-4P  
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT  
(Reactant or reagent)  
(intermediate; prepn. of biaryl phosphine and amine ligands for  
improved palladium-catalyzed amination reactions, Suzuki couplings,  
arylations, vinylations, and carbon-oxygen bond formation reactions)

IT 213697-53-1P  
RL: CAT (Catalyst use); RCT (Reactant); SPN (Synthetic preparation); PREP  
(Preparation); RACT (Reactant or reagent); USES (Uses)  
(prepd. catalyst; prepn. of biaryl phosphine and amine ligands for  
improved palladium-catalyzed amination reactions, Suzuki couplings,  
arylations, vinylations, and carbon-oxygen bond formation reactions)

IT 224311-51-7P, 2-(Di-tert-butylphosphino)biphenyl 224311-52-8P  
224311-54-0P 224311-55-1P 251320-85-1P, 2-(Dicyclohexylphosphino)-2'-  
isopropylbiphenyl 251320-86-2P, 2-(Dicyclohexylphosphino)-2'-  
methylbiphenyl 255835-81-5P 255835-82-6P 255835-83-7P,  
2-(Di-t-butylphosphino)-4'-(trifluoromethyl)biphenyl 255835-84-8P,  
2-(Di-t-butylphosphino)-2'-(isopropyl)biphenyl 255835-85-9P  
255836-32-9P 255836-65-8P 255836-67-0P 255836-68-1P,  
1-[2-(Dicyclohexylphosphino)phenyl]naphthalene 255836-69-2P,  
1-[2-(Di-t-butylphosphino)phenyl]naphthalene 255882-14-5P  
RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation);  
USES (Uses)  
(prepd. catalyst; prepn. of biaryl phosphine and amine ligands for  
improved palladium-catalyzed amination reactions, Suzuki couplings,  
arylations, vinylations, and carbon-oxygen bond formation reactions)

IT 62-53-3, Benzenamine, reactions 75-97-8 88-05-1 88-69-7 90-04-0  
91-55-4 93-55-0, Propiophenone 95-65-8 95-68-1 95-72-7 96-22-0,  
3-Pentanone 98-54-4 98-80-6 98-86-2, reactions 99-02-5 99-90-1  
99-91-2 100-00-5, 1-Chloro-4-nitrobenzene 100-01-6, reactions  
100-42-5, reactions 100-46-9, Benzenemethanamine, reactions 100-61-8,  
reactions 103-69-5 103-88-8, 4'-Bromoacetanilide 104-92-7 104-94-9  
105-53-3, Diethyl malonate 106-38-7 106-39-8 106-41-2, 4-Bromophenol  
106-43-4 106-49-0, reactions 108-41-8 108-44-1, reactions  
108-91-8, Cyclohexanamine, reactions 108-94-1, Cyclohexanone, reactions  
109-01-3 109-04-6 109-09-1 110-89-4, Piperidine, reactions  
110-91-8, Morpholine, reactions 111-26-2, 1-Hexanamine 111-92-2  
119-61-9, Benzophenone, reactions 120-72-9, Indole, reactions 122-00-9  
122-39-4, Diphenylamine, reactions 123-75-1, Pyrrolidine, reactions  
141-97-9 280-64-8, 9-BBN 392-83-6, 2-Bromobenzotrifluoride 399-52-0  
402-43-7, 4-(Trifluoromethyl)phenyl bromide 460-00-4,  
1-Bromo-4-fluorobenzene 502-42-1, Cycloheptanone 504-02-9,  
1,3-Cyclohexanedione 529-34-0 530-93-8, .beta.-Tetralone 540-88-5,  
tert-Butyl acetate 553-94-6 556-96-7 557-93-7, 2-Bromopropene  
563-80-4 565-69-5 565-80-0 576-22-7 576-26-1 583-53-9,  
1,2-Dibromobenzene 583-55-1, 2-Bromoiodobenzene 586-77-6 588-72-7,  
trans-.beta.-Bromostyrene 590-15-8, trans-1-Bromopropene 591-20-8  
592-41-6, 1-Hexene, reactions 615-36-1, 2-Bromoaniline 618-45-1  
618-89-3 619-42-1 623-00-7, 4-Bromobenzonitrile 623-03-0 623-12-1  
624-31-7 626-55-1, 3-Bromopyridine 626-60-8, 3-Chloropyridine  
645-36-3 765-30-0, Cyclopropylamine 766-51-8 766-84-7 778-82-5  
782-17-2 872-31-1, 3-Bromothiophene 873-32-5, 2-Chlorobenzonitrile  
930-29-0, 1-Chlorocyclopentene 931-51-1, Cyclohexylmagnesium chloride  
948-65-2 1003-09-4, 2-Bromothiophene 1013-88-3, Benzophenone imine  
1079-66-9, Chlorodiphenylphosphine 1122-91-4, 4-Bromobenzaldehyde  
1122-95-8 1126-46-1 1450-65-3 1590-08-5 2038-03-1,

|    |   |  |                                      |                              |                         |
|----|---|--|--------------------------------------|------------------------------|-------------------------|
|    | 4-Morpholineethanamine  | 2052-07-5,                                 | 2-Bromobiphenyl                      | 2142-68-9,                   |                         |
|    | 2'-Chloroacetophenone   | 2398-37-0                                  | 2635-13-4                            | 2845-89-8                    | 2856-63-5,              |
|    | 2-Chlorobenzyl cyanide  | 2905-65-9                                  | 3972-65-4,                           | 1-Bromo-4-t-butylbenzene     |                         |
|    | 4079-52-1   | 4541-32-6                                  | 5350-57-2                            | 5619-07-8,                   | DL-Phenylalanine methyl |
|    | ester hydrochloride   | 5720-06-9                                  | 5798-75-4,                           | Ethyl 4-bromobenzoate        |                         |
|    | 5892-99-9   | 6781-98-2                                  | 7051-16-3                            | 7073-94-1,                   | 2-Bromoisopropylbenzene |
|    | 7524-50-7,  | L-Phenylalanine methyl ester hydrochloride |                                      | 7598-28-9                    |                         |
|    | 13716-10-4,   | Chlorodi-tert-butylphosphine               | 13922-41-3,                          | 1-Naphthylboronic            |                         |
|    | acid  | 15499-27-1                                 | 16081-16-6                           | 16419-60-6                   | 16523-54-9,             |
|    | Chlorodicyclohexylphosphine   | 17496-14-9,                                | 2-Methylindanone                     | 17763-70-1                   |                         |
|    | 17763-80-3  | 17789-14-9,                                | 2-(3-Bromophenyl)1,3-dioxolane       | 17933-03-8                   |                         |
|    | 18982-54-2,   | 2-Bromobenzyl alcohol                      | 22237-13-4,                          | 4-Ethoxyphenylboronic acid   |                         |
|    | 22867-74-9  | 24544-04-5                                 | 27505-78-8                           | 27752-24-5                   | 36800-95-0,             |
|    | 4-Cyanophenyl tosylate  | 40138-16-7,                                | 2-Formylphenylboronic acid           |                              |                         |
|    | 41085-43-2,   | 2-Bromo-3-nitrotoluene                     | 41492-05-1                           | 42371-64-2                   | 53847-33-9              |
|    | 66107-29-7  | 66107-32-2                                 | 74866-28-7,                          | 2,2'-Dibromo-1,1'-binaphthyl |                         |
|    | 100379-00-8   | 100717-47-3                                | 109613-00-5                          | 112042-84-9                  | 154318-75-9             |
|    | 157282-19-4   | 158266-43-4                                | 204841-19-0,                         | 3-Acetylphenylboronic acid   |                         |
|    | 207611-58-3   | 255837-20-8                                | 255837-21-9                          | 255837-22-0                  | 255837-23-1             |
|    | RL: RCT (Reactant); RACT (Reactant or reagent)  |  |                                      |                              |                         |
|    | (starting material; prepn. of biaryl phosphine and amine ligands for improved palladium-catalyzed amination reactions, Suzuki couplings, arylations, vinylations, and carbon-oxygen bond formation reactions) |  |                                      |                              |                         |
| IT | 78235-91-3P   | 213697-67-7P                               |                                      |                              |                         |
|    | RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)   |  |                                      |                              |                         |
|    | (starting material; prepn. of biaryl phosphine and amine ligands for improved palladium-catalyzed amination reactions, Suzuki couplings, arylations, vinylations, and carbon-oxygen bond formation reactions) |  |                                      |                              |                         |
| IT | 251320-80-6P, N-(Diphenylmethylene)-2-bromoaniline  |  |                                      |                              |                         |
|    | RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)   |  |                                      |                              |                         |
|    | (synthetic product; prepn. of biaryl phosphine and amine ligands for improved palladium-catalyzed amination reactions, Suzuki couplings, arylations, vinylations, and carbon-oxygen bond formation reactions) |  |                                      |                              |                         |
| IT | 86-26-0P  | 92-69-3P, 4-Hydroxybiphenyl                | 92-91-1P, 4-Acetyl biphenyl          |                              |                         |
|    | 92-93-3P, 4-Nitrobiphenyl   | 101-70-2P, 4,4'-Dimethoxydiphenylamine     |                                      |                              |                         |
|    | 121-00-6P   | 613-37-6P, 4-Methoxybiphenyl               | 620-83-7P                            | 620-93-9P,                   |                         |
|    | Di-p-tolylamine   | 644-08-6P, 4-Methylbiphenyl                | 720-75-2P,                           | Methyl                       |                         |
|    | 4-phenylbenzoate  | 730-11-0P, 4-Methoxy-4'-nitrodiphenylamine | 774-52-7P,                           |                              |                         |
|    | N-(4-Methylphenyl)piperidine  | 825-54-7P                                  | 825-55-8P,                           | 2-Phenylthiophene            |                         |
|    | 1208-86-2P  | 1625-92-9P, 4-t-Butylbiphenyl              | 2142-66-7P,                          | 2-Acetyl biphenyl            |                         |
|    | 2920-38-9P, 4-Cyanobiphenyl   | 2928-43-0P,                                | 2-(Hydroxymethyl)biphenyl            |                              |                         |
|    | 3077-16-5P, N-(4-Methylphenyl)morpholine  | 3470-65-3P                                 | 3976-34-9P,                          |                              |                         |
|    | 2,6-Dimethylbiphenyl  | 4036-43-5P                                 | 4075-79-0P,                          | N-Acetyl-4-aminobiphenyl     |                         |
|    | 4316-51-2P, N-(4-Methoxyphenyl)-N,N-diphenylamine   | 4316-53-4P                                 |                                      |                              |                         |
|    | 4496-49-5P  | 4787-76-2P, N-(2-Methoxyphenyl)pyrrolidine | 5031-78-7P                           |                              |                         |
|    | 5405-15-2P, N-Benzyl-p-toluidine  | 5405-19-6P                                 | 6574-15-8P,                          |                              |                         |
|    | N-(4-Nitrophenyl)piperidine   | 6935-27-9P,                                | N-Benzyl-2-aminopyridine             |                              |                         |
|    | 7372-85-2P, 2,5-Dimethylbiphenyl  | 10273-87-7P                                | 10282-31-2P,                         |                              |                         |
|    | N-(4-Cyanophenyl)morpholine   | 15359-99-6P                                | 15360-00-6P                          | 16251-99-3P                  |                         |
|    | 16819-50-4P, N-(2,6-Dimethylphenyl)benzylamine  | 17057-88-4P,                               |                                      |                              |                         |
|    | 3,5-Dimethylbiphenyl  | 17952-07-7P                                | 19853-10-2P,                         | [1,1'-Biphenyl]-2-           |                         |
|    | acetonitrile  | 21218-94-0P                                | 23600-89-7P                          | 23676-05-3P                  | 23699-65-2P,            |
|    | N-(3-Acetylphenyl)aniline   | 23951-29-3P                                | 24255-25-2P,                         |                              |                         |
|    | N-(2-Pyridyl)morpholine   | 25539-14-4P                                | 25699-92-7P,                         | N-(4-                        |                         |
|    | Cyanophenyl)indole  | 25700-23-6P,                               | N-(3-Pyridyl)indole                  | 27347-14-4P                  |                         |
|    | 31144-33-9P   | 31603-95-9P,                               | 4-tert-Butyl-1-tert-butylxybenzene   |                              |                         |
|    | 34160-16-2P   | 35393-20-5P,                               | N-(Diphenylmethylene)-4-nitroaniline |                              |                         |
|    | 38158-65-5P   | 38869-05-5P                                | 39253-43-5P                          | 39910-98-0P,                 |                         |
|    | N-(4-Acetylphenyl)morpholine  | 50798-94-2P,                               | N-(2-Methoxyphenyl)benzylamine       |                              |                         |
|    | 50910-08-2P, N-(2-Pyridyl)-N,N-diphenylamine  | 51580-77-9P                                | 51786-49-3P                          |                              |                         |
|    | 52351-44-7P, N-(4-Methoxyphenyl)-2-phenylindole   | 54480-44-3P,                               |                                      |                              |                         |

4-Methoxy-4'-(dimethylamino)diphenylamine 54660-04-7P,  
 N-(4-Methoxyphenyl)pyrrolidine 55251-46-2P 56052-33-6P 56506-60-6P,  
 N-(4-Methylphenyl)hexylamine 56915-80-1P, 1-(3-Acetylphenyl)-4-methylpiperazine 60893-66-5P 61394-81-8P 62787-14-8P 62787-15-9P  
 62790-83-4P 62790-85-6P 68856-26-8P 70945-85-6P 75201-55-7P  
 75934-30-4P 76650-29-8P, 4-Acetyl-3'-methylbiphenyl 76708-72-0P  
 76708-78-6P, 2,5,3'-Trimethylbiphenyl 77422-28-7P 81693-80-3P,  
 4-Hexylanisole 82749-62-0P 83188-35-6P 84736-47-0P,  
 N-(4-t-Butylphenyl)morpholine 84736-54-9P, 2-(4-Methoxyphenyl)-3-pentanone 84839-92-9P 84839-93-0P 91949-95-0P, 4-Isopropoxybenzonitrile 92495-53-9P, 4-Methyl-2'-methoxybiphenyl 92670-29-6P, N-(3-Pyridyl)morpholine 93597-01-4P, N-(4-Methoxyphenyl)indole 94540-42-8P 94959-58-7P 97053-04-8P  
 97413-60-0P 114081-08-2P 114772-53-1P 116267-90-4P,  
 N-(3-Thiophenyl)-N,N-diphenylamine 123324-87-8P 124043-95-4P  
 129644-26-4P 137445-01-3P 138900-16-0P, N-(4-Fluorophenyl)indole 138900-19-3P 146803-96-5P 167283-32-1P, N-(4-Methylphenyl)indole 171092-38-9P, 3-(3-Acetylphenyl)pyridine 172878-95-4P 174307-96-1P  
 175696-73-8P, N-(3-Cyanophenyl)pyrrolidine 179487-70-8P 180336-54-3P,  
 N-(2,5-Dimethylphenyl)-N-methylaniline 183135-51-5P,  
 N-Methyl-N-(3-pyridyl)aniline 183135-52-6P 185259-34-1P,  
 N-(4-t-Butylphenyl)piperidine 188026-55-3P, N,N-Dibutyl-4-t-butylaniline 188026-64-4P, N-Ethyl-N-(3,5-dimethylphenyl)aniline 188026-74-6P  
 196604-19-0P 196604-21-4P 196604-24-7P 197172-67-1P 197172-69-3P  
 197640-99-6P 202802-70-8P 211292-60-3P 211292-66-9P,  
 2,6-Diisopropyl-2',6'-dimethyldiphenylamine 212382-74-6P 213014-13-2P  
 213697-51-9P 213697-52-0P, 2,6-Dimethyl-N-hexylaniline 213697-65-5P,  
 1,1-Bis(4-methylphenyl)-3-methyl-2-butanone 213697-66-6P 215394-88-0P  
 223248-27-9P 223655-23-0P 224311-62-0P 224311-63-1P 224311-65-3P  
 224311-66-4P 224311-67-5P 224311-68-6P 224311-69-7P 224311-70-0P  
 224311-72-2P 224311-73-3P 224311-74-4P 224311-75-5P 224311-76-6P  
 226569-78-4P 226917-75-5P, N-(4-Cyanophenyl)hexylamine 247940-07-4P,  
 N-Methyl-N-(3,5-dimethoxyphenyl)aniline 247940-08-5P 251320-76-0P  
 251320-77-1P, 4-Formyl-4'-ethoxybiphenyl 251320-78-2P 251320-79-3P  
 251320-81-7P, 3-Acetyl-3',5'-dimethoxybiphenyl 251320-82-8P  
 251320-83-9P 251320-84-0P, 2-Methoxy-2'-acetyl biphenyl 253768-96-6P,  
 N-(3-Cyanophenyl)benzylamine 255835-86-0P 255835-87-1P 255835-88-2P  
 255835-89-3P 255835-90-6P 255835-91-7P, N-(2,6-Dimethylphenyl)morpholine 255835-92-8P 255835-93-9P,  
 N-(4-t-Butylphenyl)benzylamine 255835-94-0P, N-(3,4-Dimethylphenyl)pyrrolidine 255835-95-1P, 2-Methoxy-4'-cyanodiphenylamine 255835-96-2P 255835-97-3P 255835-98-4P 255835-99-5P 255836-00-1P  
 255836-01-2P 255836-02-3P 255836-04-5P, N-(2-Methoxyphenyl)-N-(3-methoxyphenyl)-N-(4-methoxyphenyl)amine 255836-06-7P,  
 N-(4-Dimethylaminophenyl)-N-(4-methoxyphenyl)-N-(3-methylphenyl)amine 255836-08-9P, N-(2,4-Dimethylphenyl)-N-(4-methoxyphenyl)-N-(3-methylphenyl)amine 255836-10-3P 255836-12-5P 255836-14-7P,  
 N-(4-Butylphenyl)-N-(4-methoxyphenyl)-N-(4-methylphenyl)amine 255836-15-8P, N-(2,5-Dimethylphenyl)-N-(3,5-dimethylphenyl)-N-(4-methylphenyl)amine 255836-17-0P 255836-19-2P, N-(4-tert-Butylphenyl)indole 255836-21-6P 255836-23-8P, N-Cyclopropyl-4-tert-butylaniline 255836-25-0P, N-Cyclopropyl-2,5-dimethylaniline 255836-28-3P 255836-30-7P 255836-36-3P 255836-38-5P 255836-39-6P  
 255836-41-0P 255836-43-2P 255836-44-3P 255836-45-4P, 2-Methyl-4-(4-butylphenyl)-3-pentanone 255836-46-5P 255836-48-7P  
 255836-50-1P 255836-52-3P 255836-54-5P, 2-(3-Hydroxyphenyl)-3-pentanone 255836-56-7P, 2,4-Dimethyl-2-(4-t-butylphenyl)-3-pentanone 255836-57-8P 255836-59-0P 255836-61-4P 255836-63-6P 255836-70-5P,  
 N-(4-t-Butylphenyl)-2-phenylindole 255836-72-7P 255836-74-9P, N-(3,5-Dimethylphenyl)-2,3-dimethylindole 255836-76-1P,  
 N-(4-t-Butylphenyl)-2,3,7-trimethylindole 255836-78-3P 255836-80-7P,  
 N-(2-Pyridyl)-7-ethylindole 255836-82-9P, N-(3,5-Dimethylphenyl)-7-ethylindole 255836-84-1P 255836-86-3P 255836-88-5P 255836-90-9P

255836-92-1P 255836-94-3P 255836-95-4P 255836-96-5P 255836-97-6P  
 255836-98-7P 255836-99-8P 255837-00-4P 255837-01-5P 255837-02-6P  
 255837-03-7P

RL: SPN (Synthetic preparation); PREP (Preparation)

(synthetic product; prepn. of biaryl phosphine and amine ligands for improved palladium-catalyzed amination reactions, Suzuki couplings, arylations, vinylations, and carbon-oxygen bond formation reactions)

IT 255837-04-8P 255837-05-9P 255837-06-0P 255837-07-1P 255837-08-2P  
 255837-09-3P 255837-10-6P 255837-11-7P 255837-12-8P 255837-13-9P

RL: SPN (Synthetic preparation); PREP (Preparation)  
 (synthetic product; prepn. of biaryl phosphine and amine ligands for improved palladium-catalyzed amination reactions, Suzuki couplings, arylations, vinylations, and carbon-oxygen bond formation reactions)

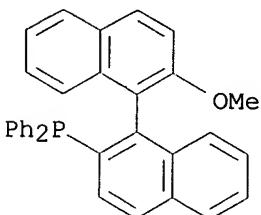
IT 145964-33-6

RL: CAT (Catalyst use); USES (Uses)

(catalyst; prepn. of biaryl phosphine and amine ligands for improved palladium-catalyzed amination reactions, Suzuki couplings, arylations, vinylations, and carbon-oxygen bond formation reactions)

RN 145964-33-6 HCAPLUS

CN Phosphine, [(1R)-2'-methoxy[1,1'-binaphthalen]-2-yl]diphenyl- (9CI) (CA INDEX NAME)



L81 ANSWER 2 OF 18 HCAPLUS COPYRIGHT 2003 ACS

AN 1998:618676 HCAPLUS

DN 129:245667

TI Optically active phosphine derivative having at least two vinyl groups, polymer produced using the same as monomer and transition metal complexes of these

IN Tamao, Kyoko; Itoi, Yohei

PA Takasago International Corp., Japan

SO Eur. Pat. Appl., 26 pp.

CODEN: EPXXDW

DT Patent

LA English

IC ICM C07F009-6574

ICS C07F015-00; C08F030-02; C08F030-04; C07C045-50; C07B053-00

ICI C07M007-00

CC 35-3 (Chemistry of Synthetic High Polymers)

FAN.CNT 1

| PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|------------|------|------|-----------------|------|
|------------|------|------|-----------------|------|

|              |    |          |                |              |
|--------------|----|----------|----------------|--------------|
| PI EP 864577 | A2 | 19980916 | EP 1998-301763 | 19980310 <-- |
| EP 864577    | A3 | 19990825 |                |              |
| EP 864577    | B1 | 20030205 |                |              |

R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT,  
 IE, SI, LT, LV, FI, RO

|             |    |          |               |              |
|-------------|----|----------|---------------|--------------|
| JP 10251282 | A2 | 19980922 | JP 1997-72817 | 19970311 <-- |
|-------------|----|----------|---------------|--------------|

|            |   |          |               |              |
|------------|---|----------|---------------|--------------|
| US 6143834 | A | 20001107 | US 1998-38280 | 19980311 <-- |
|------------|---|----------|---------------|--------------|

|            |    |          |                |              |
|------------|----|----------|----------------|--------------|
| US 6248848 | B1 | 20010619 | US 2000-603991 | 20000627 <-- |
|------------|----|----------|----------------|--------------|

|                    |    |              |  |  |
|--------------------|----|--------------|--|--|
| PRAI JP 1997-72817 | A  | 19970311 <-- |  |  |
| US 1998-38280      | A3 | 19980311 <-- |  |  |

OS MARPAT 129:245667

AB Specified 2'-diarylphosphino-1,1'-biphenyl-2-yloxy(6,6'-divinyl-1,1'-binaphthalene -2,2'-diyloxy)phosphine derivs. are useful in polymers and transition metal complexes. Also disclosed are a polymer having structural units derived from the phosphine deriv. and a transition metal complex obtained by causing a transition metal compd. to act on the phosphine deriv. or the polymer. A novel polymer-supported ligand is provided which, when used as a catalyst for asym. syntheses, gives satisfactory results concerning catalytic activity, enantiomer excess, etc.

ST optically active phosphine deriv polymer; transition metal complex phosphine polymer

IT Hydroformylation catalysts  
 (optically active phosphine deriv. having at least two vinyl groups, polymer produced using the same as monomer and transition metal complexes of these)

IT 100-42-5DP, hydroformylated 14874-82-9DP, Rhodium dicarbonylacetylacetone, complexes with 2'-diarylphosphino-1,1'-biphenyl-2-yloxy(6,6'-divinyl-1,1'-binaphthalene -2,2'-diyloxy)phosphine polymers 213188-62-6P 213188-64-8P  
 RL: IMF (Industrial manufacture); PREP (Preparation)  
 (optically active phosphine deriv. having at least two vinyl groups, polymer produced using the same as monomer and transition metal complexes of these)

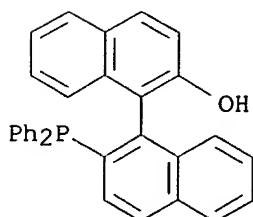
IT 80655-81-8P 126613-06-7P 132532-04-8P 132548-91-5P  
**149917-88-4P** 187742-81-0P 205238-73-9P 205238-75-1P  
 213314-12-6P 213314-13-7P 213314-14-8P 213314-15-9P 213314-16-0P  
**213314-17-1P** **213314-18-2P**  
 RL: IMF (Industrial manufacture); RCT (Reactant); PREP (Preparation); RACT (Reactant or reagent)  
 (optically active phosphine deriv. having at least two vinyl groups, polymer produced using the same as monomer and transition metal complexes of these)

IT 68-12-2, Dimethylformamide, reactions 358-23-6, Trifluoromethanesulfonic anhydride 6737-42-4, 1,3-Bis(diphenylphosphino)propane 7726-95-6, Bromine, reactions 18531-94-7 18531-99-2 69739-34-0, Tert-Butyldimethylsilyl triflate  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (optically active phosphine deriv. having at least two vinyl groups, polymer produced using the same as monomer and transition metal complexes of these)

IT **149917-88-4P** **213314-17-1P** **213314-18-2P**  
 RL: IMF (Industrial manufacture); RCT (Reactant); PREP (Preparation); RACT (Reactant or reagent)  
 (optically active phosphine deriv. having at least two vinyl groups, polymer produced using the same as monomer and transition metal complexes of these)

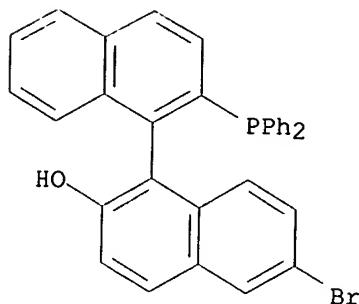
RN 149917-88-4 HCPLUS

CN [1,1'-Binaphthalen]-2-ol, 2'-(diphenylphosphino)-, (1R)- (9CI) (CA INDEX NAME)



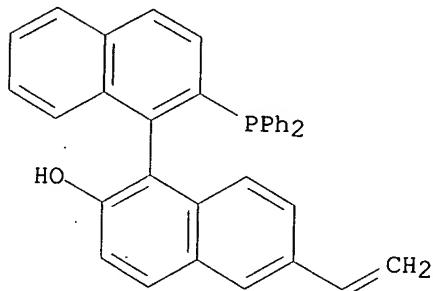
RN 213314-17-1 HCPLUS

CN [1,1'-Binaphthalen]-2-ol, 6-bromo-2'-(diphenylphosphino)-, (1R)- (9CI)  
 (CA INDEX NAME)



RN 213314-18-2 HCAPLUS

CN [1,1'-Binaphthalen]-2-ol, 2'-(diphenylphosphino)-6-ethenyl-, (1R)- (9CI)  
 (CA INDEX NAME)



L81 ANSWER 3 OF 18 HCAPLUS COPYRIGHT 2003 ACS

AN 1998:614290 HCAPLUS

DN 129:316694

TI Preparation of vinyl-containing chiral phosphines, their polymers, and their transition metal complexes as catalysts for asymmetric hydroformylation

IN Tamao, Kyoko; Itoi, Yohei

PA Takasago Perfumery Co., Ltd., Japan

SO Jpn. Kokai Tokkyo Koho, 13 pp.

CODEN: JKXXAF

DT Patent

LA Japanese

IC ICM C07F009-6574

ICS B01J031-24; C07F015-00; C08F012-32; C08F212-04; C08F212-36

CC 35-2 (Chemistry of Synthetic High Polymers)

Section cross-reference(s): 29, 38, 67

FAN.CNT 1

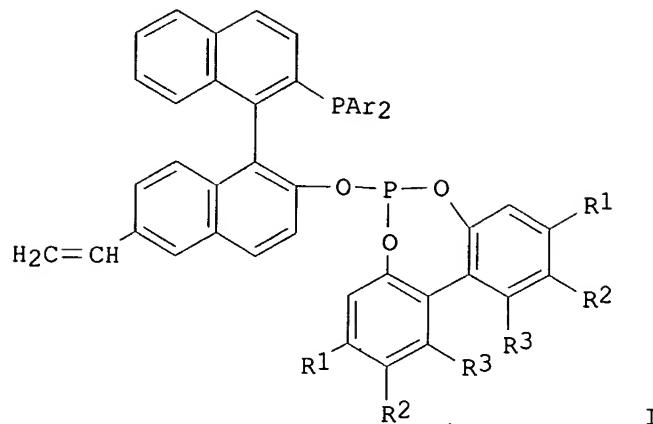
| PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|------------|------|------|-----------------|------|
|------------|------|------|-----------------|------|

|                |    |          |                |              |
|----------------|----|----------|----------------|--------------|
| PI JP 10251283 | A2 | 19980922 | JP 1997-72838  | 19970311 <-- |
| EP 877029      | A2 | 19981111 | EP 1998-301768 | 19980310 <-- |
| EP 877029      | A3 | 19990825 |                |              |
| EP 877029      | B1 | 20021211 |                |              |

R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT,  
 IE, SI, LT, LV, FI, RO

|                    |   |              |               |              |
|--------------------|---|--------------|---------------|--------------|
| US 6022936         | A | 20000208     | US 1998-38131 | 19980311 <-- |
| PRAI JP 1997-72838 | A | 19970311 <-- |               |              |

OS MARPAT 129:316694  
GI



AB Title phosphines I [Ar = (substituted) Ph, (substituted) naphthyl; R1, R2 = H, lower (halo)alkyl, lower alkoxy, halo, benzyloxy; R3 = lower (halo)alkyl, lower alkoxy, halo, benzyloxy; R2, R3 may form hydrocarbon ring], their transition metal complexes, polymers or oligomers prepd. by soln. or suspension polymn. of I, and transition metal complexes of the polymers or oligomers are prepd. Optically active R5CHMeCHO [R5 = C1-8 alkyl, (substituted) Ph, naphthyl, acetoxy, etc.] are prepd. by asym. hydroformylation of R5CH:CH2 (R5 = same as above) using the polymer transition metal complexes. Condensation of (R)-2'-diphenylphosphino-2-hydroxy-6-vinyl-1,1'-binaphthyl (prepn. given) with (S)-1,1'-binaphthalene-2,2'-dioxychlorophosphine in ether in the presence of Et<sub>3</sub>N at room temp. for 24 h gave 69% optically active I (Ar = Ph, R1 = H, R2-R3 = CH:CHCH:CH), which was polymd. with styrene and divinylbenzene and treated with Rh(acac)(CO)<sub>2</sub> to give a complex. Styrene was hydroformylated by CO and H in C<sub>6</sub>H<sub>6</sub> using the complex at 60.degree. under 50 atm for 40 h to give PhCHMeCHO with 94% selectivity and 82% ee optical purity at 97% conversion.

ST chiral phosphine polymer complex catalyst; styrene asym hydroformylation catalyst phosphine polymer; aldehyde prepn asym hydroformylation olefin; transition metal complex phosphine polymer catalyst; vinyl binaphthylphosphine polymer complex catalyst

IT Hydroformylation catalysts  
(asym.; prepn. of vinyl-contg. chiral phosphines for polymeric transition metal complexes as catalysts for asym. hydroformylation)

IT Aldehydes, preparation  
RL: IMF (Industrial manufacture); SPN (Synthetic preparation); PREP (Preparation)  
(chiral; prepn. of vinyl-contg. chiral phosphines for polymeric transition metal complexes as catalysts for asym. hydroformylation)

IT Transition metal complexes  
RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation); USES (Uses)  
(phosphine; prepn. of vinyl-contg. chiral phosphines for polymeric transition metal complexes as catalysts for asym. hydroformylation)

IT Alkenes, reactions  
RL: RCT (Reactant); RACT (Reactant or reagent)  
(prepn. of vinyl-contg. chiral phosphines for polymeric transition metal complexes as catalysts for asym. hydroformylation)

IT Phosphines

RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation);  
 USES (Uses)  
 (transition metal complexes; prepn. of vinyl-contg. chiral phosphines  
 for polymeric transition metal complexes as catalysts for asym.  
 hydroformylation)

IT 7440-16-6DP, Rhodium, complexes with chiral phosphine-contg. polymer,  
 preparation 205238-71-7DP, rhodium complex  
 RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation);  
 USES (Uses)  
 (prepn. of vinyl-contg. chiral phosphines for polymeric transition  
 metal complexes as catalysts for asym. hydroformylation)

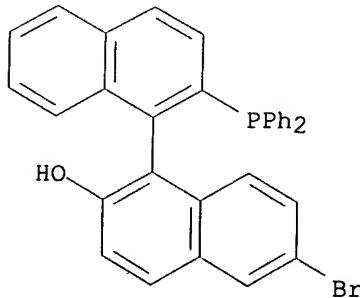
IT 93-53-8P, .alpha.-Methylphenylacetaldehyde  
 RL: IMF (Industrial manufacture); SPN (Synthetic preparation); PREP  
 (Preparation)  
 (prepn. of vinyl-contg. chiral phosphines for polymeric transition  
 metal complexes as catalysts for asym. hydroformylation)

IT 100-42-5, reactions 4559-70-0, Diphenylphosphine oxide 18531-94-7  
 137156-22-0  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (prepn. of vinyl-contg. chiral phosphines for polymeric transition  
 metal complexes as catalysts for asym. hydroformylation)

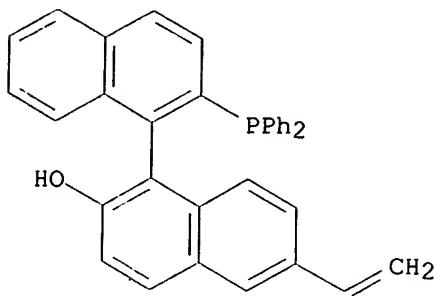
IT 126613-06-7P 132532-04-8P 132548-91-5P 205238-71-7P 213314-16-0P  
**213314-17-1P 213314-18-2P** 214913-51-6P  
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT  
 (Reactant or reagent)  
 (prepn. of vinyl-contg. chiral phosphines for polymeric transition  
 metal complexes as catalysts for asym. hydroformylation)

IT **213314-17-1P 213314-18-2P**  
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT  
 (Reactant or reagent)  
 (prepn. of vinyl-contg. chiral phosphines for polymeric transition  
 metal complexes as catalysts for asym. hydroformylation)

RN 213314-17-1 HCAPLUS  
 CN [1,1'-Binaphthalen]-2-ol, 6-bromo-2'-(diphenylphosphino)-, (1R)- (9CI)  
 (CA INDEX NAME)



RN 213314-18-2 HCAPLUS  
 CN [1,1'-Binaphthalen]-2-ol, 2'-(diphenylphosphino)-6-ethenyl-, (1R)- (9CI)  
 (CA INDEX NAME)



L81 ANSWER 4 OF 18 HCAPLUS COPYRIGHT 2003 ACS  
 AN 1997:195644 HCAPLUS

DN 126:186205

TI Preparation of chiral binaphthalene phosphine-phosphinite compounds and their use in asymmetric synthesis of 4-[(R)-1'-formylethyl]azetidin-2-one derivatives by hydroformylation

IN Saito, Takao; Matsumura, Kazuhiko; Miura, Takashi; Kumabayashi, Hidenori; Yoshida, Akifumi

PA Takasago International Corporation, Japan

SO Eur. Pat. Appl., 26 pp.

CODEN: EPXXDW

DT Patent

LA English

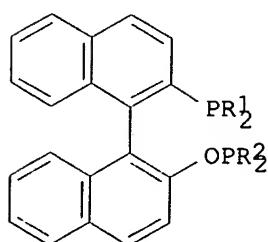
IC ICM C07F009-46

ICS C07D205-08

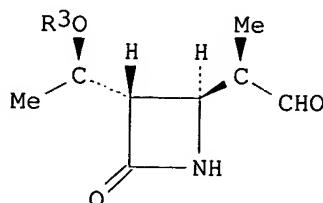
CC 29-7 (Organometallic and Organometalloidal Compounds)  
 Section cross-reference(s): 22, 27, .67

FAN.CNT 1

|      | PATENT NO.                             | KIND | DATE         | APPLICATION NO. | DATE         |
|------|--|------|--------------|-----------------|--------------|
| PI   | EP 755937                              | A1   | 19970129     | EP 1996-305182  | 19960715 <-- |
|      | EP 755937                              | B1   | 20021023     |                 |              |
|      | R: CH, DE, FR, GB, IT, LI, NL          |      |              |                 |              |
|      | JP 09040684                            | A2   | 19970210     | JP 1995-210215  | 19950727 <-- |
|      | US 5824822                             | A    | 19981020     | US 1996-677226  | 19960709 <-- |
| PRAI | JP 1995-210215                         | A    | 19950727 <-- |                 |              |
| OS   | CASREACT 126:186205; MARPAT 126:186205 |      |              |                 |              |
| GI   |  |      |              |                 |              |



I



II

AB Phosphine-phosphinite compds. (R)-I (R1, R2 = substituted or unsubstituted Ph, naphthyl) and a process for prep. a 4-[(R)-1'-formylethyl]azetidin-2-one deriv. II (R3 = H, protective group for a hydroxyl group) using (R)-I are claimed. (R)-I, either in combination, or as a complex, with a transition metal compd., is useful as a catalyst for asym. hydroformylation and makes it possible to easily synthesize an important

intermediate for carbapenem antibiotics or a precursor thereof at high regioselectivity and diastereoselectivity. For example, (3S,4R)-3-((R)-1-tert-butyldimethylsilyloxy)ethyl-4-((R)-1'-formylethyl)azetidin-2-one, (3S,4R)-3-((R)-1-tert-butyldimethylsilyloxy)ethyl-4-((S)-1'-formylethyl)azetidin-2-one, and (3S,4R)-3-((R)-1-tert-butyldimethylsilyloxy)ethyl-4-(2-formylethyl)azetidin-2-one were formed in 68.4/3.6/28 ratio and, after chromatog., a 68% yield of the 1st 2 compds. with 95/5 isomer ratio was obtained in the presence of (R)-I (R1 = 3,5-dimethylphenyl; R2 = Ph) and [Rh(COD)Cl]2; other phosphine-phosphinite compds. such as (R)-I (R1 = Ph; R2 = OPh) gave significantly inferior results. The detailed prepn. of (R)-I (R1 = 3,5-dimethylphenyl; R2 = Ph) is given and results of catalytic tests are given for about 20 (R)-I.

ST binaphthyl phosphine phosphinite metal hydroformylation catalyst; vinylazetidinone asym hydroformylation catalyst; formylethylazetidinone asym synthesis hydroformylation catalyst; azetidinone formylethyl asym synthesis; chiral binaphthalene phosphine phosphinite hydroformylation catalyst

IT Hydroformylation catalysts  
(asym., regioselective; binaphthyl phosphine-phosphinite compds. in combination or as complex with transition metal compd. for vinylazetidinone)

IT Asymmetric synthesis and induction  
(of (formylethyl)azetidinone in presence of binaphthyl phosphine-phosphinite compds. in combination or as complex with transition metal compd.)

IT Regiochemistry  
Stereochemistry  
(of hydroformylation of vinylazetidinone in presence of binaphthyl phosphine-phosphinite compds. in combination or as complex with transition metal compd.)

IT 112256-72-1  
RL: RCT (Reactant); RACT (Reactant or reagent)  
(asym. hydroformylation in presence of binaphthalene phosphine-phosphinite compds. in combination or as complex with transition metal compd.)

IT 159496-98-7P  
RL: SPN (Synthetic preparation); PREP (Preparation)  
(asym. synthesis in presence of binaphthalene phosphine-phosphinite compds. in combination or as complex with transition metal compd.)

IT 12092-47-6, Bis(chloro(1,5-cyclooctadiene)rhodium) 14874-82-9,  
(Acetylacetato)dicarbonylrhodium  
RL: CAT (Catalyst use); USES (Uses)  
(asym. synthesis of (formylethyl)azetidinone in presence of binaphthalene phosphine-phosphinite compds. in combination or as complex with transition metal compd.)

IT 183119-22-4P 183119-23-5P 183119-24-6P 187461-34-3P 187461-37-6P  
187461-39-8P 187461-41-2P 187461-43-4P 187461-44-5P 187461-45-6P  
187461-46-7P 187461-47-8P 187461-48-9P 187461-49-0P 187461-50-3P  
187461-51-4P 187461-52-5P 187461-53-6P 187461-54-7P  
**187461-55-8P 187461-56-9P**  
RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation);  
USES (Uses)  
(binaphthalene phosphine-phosphinite compd. in combination or as complex with transition metal compd. for asym. synthesis of (formylethyl)azetidinone)

IT 358-23-6, Trifluoromethanesulfonic anhydride 556-96-7, 5-Bromo-m-xylene  
762-04-9, Diethyl phosphite 1019-71-2, Chlorobis(4-methylphenyl)phosphine 1079-66-9, Chlorodiphenylphosphine 4559-70-0, Diphenylphosphine oxide 13685-24-0, Chlorobis(4-(trifluoromethyl)phenyl)phosphine 18531-94-7, (R)-1,1'-Bi-2-naphthol 23039-97-6, Chlorobis(4-fluorophenyl)phosphine 30309-80-9, Bis(o-tolyl)phosphine oxide 74289-57-9, Chlorobis(3,5-

dimethylphenyl)phosphine 78871-05-3, Bis(2-naphthyl)phosphine oxide 142421-57-6, Bis(3,5-bis(trifluoromethyl)phenyl)(chloro)phosphine 159418-72-1, Chlorobis(3,5-difluorophenyl)phosphine 187344-92-9, Bis(3,5-dimethylphenyl)phosphine oxide 187344-93-0, Bis(6-methoxy-2-naphthyl)phosphine oxide 187344-94-1, Bis(3-biphenylyl)phosphine oxide 187344-95-2, Bis(4-biphenylyl)phosphine oxide 187344-96-3, Bis(4-(2,4,6-trimethylphenyl)phenyl)phosphine oxide 187344-97-4, Dicyclopentylphosphine oxide 187344-98-5, Bis(3,5-bis(trimethylsilyl)phenyl)phosphine oxide 187344-99-6

RL: RCT (Reactant); RACT (Reactant or reagent)  
(for prepn. of binaphthalene phosphine-phosphinite compd. for asym. hydroformylation catalysis)

IT 126613-06-7P, (R)-2,2'-Bis(trifluoromethanesulfonyloxy)-1,1'-binaphthalene 149917-89-5P 187461-57-0P 187461-58-1P

RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)  
(for prepn. of binaphthalene phosphine-phosphinite compd. for asym. hydroformylation catalysis)

IT 183119-15-5P

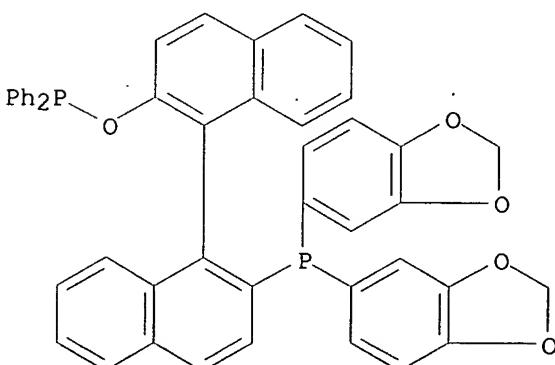
RL: SPN (Synthetic preparation); PREP (Preparation)  
(prepn. of)

IT 187461-55-8P

RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation);  
USES (Uses)  
(binaphthalene phosphine-phosphinite compd. in combination or as complex with transition metal compd. for asym. synthesis of (formylethyl)azetidinone)

RN 187461-55-8 HCPLUS

CN Phosphinous acid, diphenyl-, 2'-[bis(1,3-benzodioxol-5-yl)phosphino][1,1'-binaphthalen]-2-yl ester, (R)- (9CI) (CA INDEX NAME)

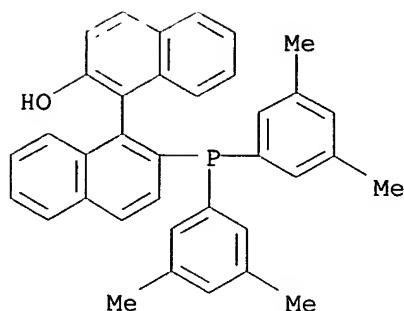


IT 149917-89-5P

RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)  
(for prepn. of binaphthalene phosphine-phosphinite compd. for asym. hydroformylation catalysis)

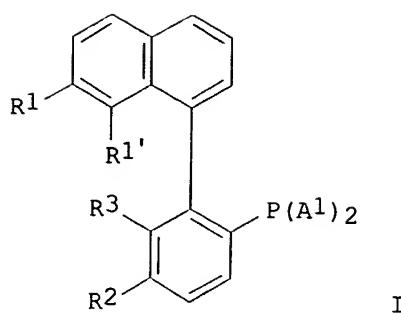
RN 149917-89-5 HCPLUS

CN [1,1'-Binaphthalen]-2-ol, 2'-[bis(3,5-dimethylphenyl)phosphino]-, (R)- (9CI) (CA INDEX NAME)



L81 ANSWER 5 OF 18 HCAPLUS COPYRIGHT 2003 ACS  
 AN 1996:610021 HCAPLUS  
 DN 125:248105  
 TI Optically active tertiary phosphine compounds, transition metal complexes comprising the same as ligands and process for preparing optically active organic silicon compounds using said transition metal complexes  
 IN Hayashi, Tamio; Minai, Masayoshi; Iwakura, Kazunori  
 PA Sumitomo Chemical Company Limited, Japan  
 SO Eur. Pat. Appl., 20 pp.  
 CODEN: EPXXDW  
 DT Patent  
 LA English  
 IC ICM C07F009-50  
     ICS B01J031-28; C07F015-00; C07F007-12  
 ICI C07M007-00  
 CC 29-7 (Organometallic and Organometalloidal Compounds)  
     Section cross-reference(s): 25, 67  
 FAN.CNT 1

|      | PATENT NO.                             | KIND | DATE         | APPLICATION NO. | DATE         |
|------|--|------|--------------|-----------------|--------------|
| PI   | EP 731105                              | A1   | 19960911     | EP 1996-103689  | 19960308 <-- |
|      | EP 731105                              | B1   | 20011205     |                 |              |
|      | R: CH, DE, GB, LI                      |      |              |                 |              |
|      | JP 08245662                            | A2   | 19960924     | JP 1995-51094   | 19950310 <-- |
|      | JP 08245663                            | A2   | 19960924     | JP 1995-51482   | 19950310 <-- |
|      | JP 09143185                            | A2   | 19970603     | JP 1996-44680   | 19960301 <-- |
|      | US 5621129                             | A    | 19970415     | US 1996-612108  | 19960307 <-- |
| PRAI | JP 1995-49685                          | A    | 19950309 <-- |                 |              |
|      | JP 1995-51094                          | A    | 19950310 <-- |                 |              |
|      | JP 1995-51482                          | A    | 19950310 <-- |                 |              |
|      | JP 1995-238204                         | A    | 19950918 <-- |                 |              |
| OS   | CASREACT 125:248105; MARPAT 125:248105 |      |              |                 |              |
| GI   |  |      |              |                 |              |



AB The prepn. of tertiary phosphine compds. I (R<sub>1</sub>, R<sub>1'</sub> = H, R<sub>1</sub>R<sub>1'</sub> = CH:CHCH:CH; R<sub>2</sub>R<sub>3</sub> = 2-CH:CHC<sub>6</sub>H<sub>4</sub>, etc.; R<sub>2</sub> = H, R<sub>3</sub> = substituted or unsubstituted alkyl, Ph group, etc.; A<sub>1</sub> = 3-trifluoromethylphenyl or 3,5-bis(trifluoromethyl)phenyl, etc.) was given. I was used as cocatalyst to prep. optically active silicon compd. Thus, (S)-3-diphenylphosphino-4,4'-biphenanthryl (prepn. given)/allylpalladium chloride dimer catalyzed silylation of styrene with trichlorosilane gave 1-phenyl-1-trichlorosilylethene. Oxidative desilylation of 1-phenyl-1-trichlorosilylethene with KF/KHCO<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> in THF/MeOH gave optically pure (R)-1-phenethyl alc. in 95% yield.

ST optically active phosphine compd prep catalyst; transition metal catalyzed optically silicon prep; asym synthesis aryl alc

IT Asymmetric synthesis and induction  
(prepn. of optically active tertiary phosphine compds. as cocatalysts for prep. optically active org. silicon compds.)

IT 85719-57-9  
RL: CAT (Catalyst use); USES (Uses)  
(Grignard phenylation of naphthylbis(trifluoromethanesulfonyloxy)benzene with phenylmagnesium bromide catalyzed by)

IT 90-11-9, 1-Bromonaphthalene  
RL: RCT (Reactant); RACT (Reactant or reagent)  
(borylation of)

IT 121-43-7, Trimethoxyborane  
RL: RCT (Reactant); RACT (Reactant or reagent)  
(borylation of bromonaphthalene with)

IT 151-10-0, 1,3-Dimethoxybenzene  
RL: RCT (Reactant); RACT (Reactant or reagent)  
(bromination of)

IT 7688-25-7, 1,4-Bis(diphenylphosphino)butane  
RL: CAT (Catalyst use); USES (Uses)  
(palladium-catalyzed phosphinylation of naphthylbis(trifluoromethanesulfonyloxy)benzene with diphenylphosphine oxide in presence of)

IT 4559-70-0, Diphenylphosphine oxide  
RL: RCT (Reactant); RACT (Reactant or reagent)  
(phosphinylation of mesyloxybiphenanthryl compd. with)

IT 1517-69-7P, (R)-1-Phenethyl alcohol  
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)  
(prepn. and carbamate formation of)

IT 13922-41-3P, 1-Naphthylboric acid  
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)  
(prepn. and coupling reaction with bromodimethoxybenzene)

IT 16932-45-9P, 1-Bromo-2,6-dimethoxybenzene  
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)  
(prepn. and coupling reaction with naphthylboric acid)

IT 173300-93-1P, 1-Naphthyl-2,6-dimethoxybenzene

RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)  
 (prep. and demethylation of)

IT 170647-33-3P 181934-58-7P, (S)-3-Diphenylphosphinyl-4,4'-biphenanthryl  
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)  
 (prep. and deoxygenation of)

IT 7726-28-5P  
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)  
 (prep. and oxidative desilylation of)

IT 181934-55-4P  
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)  
 (prep. and palladium catalyzed hydrogenation of)

IT 170647-24-2P, 1-Naphthyl-2,6-bis(trifluoromethanesulfonyloxy)benzene  
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)  
 (prep. and palladium-catalyzed phenylation of)

IT 170647-29-7P 181934-57-6P  
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)  
 (prep. and phosphinylation of)

IT 100838-76-4P, (R)-(-)-3,3'-Dihydroxy-4,4'-biphenanthryl 173300-94-2P,  
 1-Naphthyl-2,6-dihydroxybenzene 181934-56-5P, (S)-3-Hydroxy-4,4'-  
 biphenanthryl  
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)  
 (prep. and trifluoromethanesulfonylation of)

IT 17995-58-3P 18035-34-2P 58276-68-9P 100838-77-5P,  
 (S)-(+)-3,3'-Dihydroxy-4,4'-biphenanthryl 159241-56-2P 181934-63-4P,  
 3,5-Dinitrophenyl carbamate 181934-73-6P 181934-75-8P 181934-77-0P.  
 181934-99-6P 181935-04-6P 181935-08-0P 181935-10-4P  
 RL: SPN (Synthetic preparation); PREP (Preparation)  
 (prep. of)

IT 12012-95-2, Allylpalladium chloride dimer 145964-33-6  
 RL: CAT (Catalyst use); USES (Uses)  
 (prep. of optically active tertiary phosphine compds. as cocatalysts  
 for prep. optically active org. silicon compds.)

IT 156456-77-8P 170647-35-5P 181934-60-1P, (S)-3-Diphenylphosphino-4,4'-  
 biphenanthryl 181934-89-4P 181934-90-7P 181934-92-9P 181934-94-1P  
 RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation);  
 USES (Uses)  
 (prep. of optically active tertiary phosphine compds. as cocatalysts  
 for prep. optically active org. silicon compds.)

IT 100-42-5, reactions 402-24-4, 3-Trifluoromethylphenylethene 402-50-6,  
 4-Trifluoromethylphenylethene 586-39-0, 3-Nitrophenylethene 611-15-4,  
 2-Methylphenylethene 622-97-9 637-50-3, 1-Phenylpropene 637-69-4  
 828-15-9, 1-Phenyl-1-hexene 1073-67-2, 4-Chlorophenylethene 2039-82-9,  
 4-Bromophenylethene 2039-85-2, 3-Chlorophenylethene 10025-78-2,  
 Trichlorosilane 15929-44-9 15979-14-3 18531-94-7  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (prep. of optically active tertiary phosphine compds. as cocatalysts  
 for prep. optically active org. silicon compds.)

IT 181934-84-9P  
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)  
 (prep. of optically active tertiary phosphine compds. as cocatalysts  
 for prep. optically active org. silicon compds.)

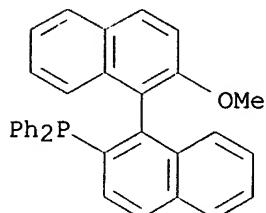
IT 66478-70-4, 3,3'-Dihydroxy-4,4'-biphenanthryl  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (racemic; optical resoln. of)

IT 145964-33-6

RL: CAT (Catalyst use); USES (Uses)  
 (prepn. of optically active tertiary phosphine compds. as cocatalysts  
 for prep. optically active org. silicon compds.)

RN 145964-33-6 HCPLUS

CN Phosphine, [(1R)-2'-methoxy[1,1'-binaphthalen]-2-yl]diphenyl- (9CI) (CA  
 INDEX NAME)



L81 ANSWER 6 OF 18 HCPLUS COPYRIGHT 2003 ACS

AN 1996:447108 HCPLUS

DN 125:143006

TI Preparation of phosphine compounds as cocatalysts and their complexes as catalysts for producing optically active aldehyde or the use of 4-[(R)-1'-formylethyl]azetidin-2-one derivatives as cocatalysts

IN Takaya, Hidemasa; Sakai, Nozomu; Tamao, Kyoko; Mano, Satoshi; Kumobayashi, Hidenori; Tomita, Tetsuo; Saito, Takao; Matsumura, Kazuhiko; Kato, Yasushi; Sayo, Noboru

PA Takasago International Corp., Japan

SO U.S., 29 pp., Cont.-in-part of U.S. Ser. No. 209,069, abandoned.  
 CODEN: USXXAM

DT Patent

LA English

IC ICM C07F015-00

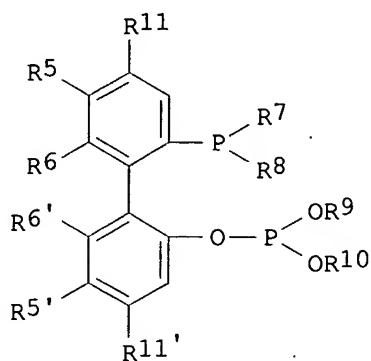
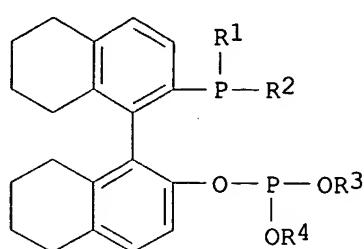
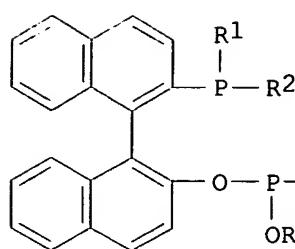
ICS C07F009-02

NCL 556018000

CC 29-7 (Organometallic and Organometalloidal Compounds)  
 Section cross-reference(s): 21, 67

FAN.CNT 5

|      | PATENT NO.                             | KIND | DATE         | APPLICATION NO. | DATE         |
|------|--|------|--------------|-----------------|--------------|
| PI   | US 5530150                             | A    | 19960625     | US 1994-323492  | 19941012 <-- |
|      | JP 06263776                            | A2   | 19940920     | JP 1993-52538   | 19930312 <-- |
|      | JP 3313805                             | B2   | 20020812     |                 |              |
|      | JP 06263681                            | A2   | 19940920     | JP 1993-52539   | 19930312 <-- |
|      | JP 06263777                            | A2   | 19940920     | JP 1993-52540   | 19930312 <-- |
|      | JP 2002128759                          | A2   | 20020509     | JP 2001-328632  | 19940301 <-- |
| PRAI | JP 1993-52538                          | A    | 19930312 <-- |                 |              |
|      | JP 1993-52539                          | A    | 19930312 <-- |                 |              |
|      | JP 1993-52540                          | A    | 19930312 <-- |                 |              |
|      | JP 1993-77484                          | A    | 19930312 <-- |                 |              |
|      | US 1994-208378                         | B2   | 19940310 <-- |                 |              |
|      | US 1994-209051                         | B2   | 19940311 <-- |                 |              |
|      | US 1994-209069                         | B2   | 19940311 <-- |                 |              |
|      | US 1994-209070                         | B2   | 19940311 <-- |                 |              |
|      | JP 1994-54426                          | A3   | 19940301 <-- |                 |              |
| OS   | CASREACT 125:143006; MARPAT 125:143006 |      |              |                 |              |
| GI   |  |      |              |                 |              |



AB The prepn. of phosphine compds. I-III (R1, R2 = same or different, each represent a Ph group or a Ph group substituted with a halogen atom or a lower alkyl group or taken together form a divalent hydrocarbon group; R3, R4 = same or different, each represent a lower alkyl group, a Ph group or a Ph group substituted with a halogen atom, a lower alkyl group or a lower alkoxy group or taken together form a divalent hydrocarbon group; R6, R6' = same or different, each represent H, lower alkyl group or lower alkoxy group; R5, R5', R11, R11' = same or different, each represent H, lower alkyl group, lower alkoxy group, halogen atom; or a pair of R5 and R6 or a pair of R5' and R6' may form a ring; R7, R8 = same or different, each represent a Ph group or a Ph group substituted with a lower alkyl group, a halogen atom or a lower alkoxy group; R9, R10 = same or different, each represent a Ph group or a Ph group substituted with a lower alkyl group, a lower alkoxy group or a halogen atom; or R9 and R10 may be taken together to form a divalent hydrocarbon group) and their transition metal complexes, useful in the prepn. of optically active aldehydes, is described. Thus, title phosphine (R)-2-diphenylphosphino-1,1'-binaphthalene-2'-yloxy-((S)-1,1'-binaphthalene-2,2'-diyldioxy)phosphine [(R,S)-BINAPHOS] prepd. in 5 steps starting from (R)-1,1'-bi-2-naphthol. [(R,S)-BINAPHOS]/Rh(CO)<sub>2</sub>(acac) catalyzed asym. hydroformylation of vinyl acetate gave 2-acetoxypropanal predominantly which upon Jones oxidn. gave (S)-(-)-2-acetoxypropionic acid with 99% enantiomeric excess.

ST phosphine ligand prepn cocatalyst asym hydroformylation; BINAPHOS prepn cocatalyst asym hydroformylation; rhodium catalyst phosphine ligand cocatalyst hydroformylation; aldehyde optically active prepn

IT Aldehydes, preparation

RL: SPN (Synthetic preparation); PREP (Preparation)  
(optically active; prepn. of phosphine compds. as cocatalysts and its complexes as catalysts for producing optically active aldehyde)

IT Asymmetric synthesis and induction

(prepn. of phosphine compds. as cocatalysts and its complexes as catalysts for producing optically active aldehyde)

IT Hydroformylation catalysts

(asym., prepn. of phosphine compds. as cocatalysts and its complexes as catalysts for producing optically active aldehyde)

IT Hydroformylation

(stereoselective, prepn. of phosphine compds. as cocatalysts and its complexes as catalysts for producing optically active aldehyde)

IT 104-53-0P, Benzenepropanal 111-71-7P, Heptanal 2436-29-5P 5406-12-2P  
 6034-46-4P, (S)-(-)-2-Acetoxypropionic acid 7782-24-3P,  
 (S)-(+)-2-Phenylpropionic acid 18545-28-3P 20401-88-1P 33204-48-7P  
 37414-44-1P 38235-74-4P 40764-03-2P 66875-69-2P 66875-71-6P  
 73365-03-4P 75677-02-0P 81292-68-4P 110773-62-1P 132151-88-3P  
 147922-82-5P 149917-84-0P 155566-54-4P 159496-97-6P 180060-81-5P  
 RL: SPN (Synthetic preparation); PREP (Preparation)  
 (prepn. of)

IT 159496-98-7P 159573-35-0P  
 RL: CAT (Catalyst use); RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent); USES (Uses)  
 (prepn. of formylethylazetidinone derivs. as cocatalysts for producing optically active aldehyde)

IT 112256-72-1  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (prepn. of formylethylazetidinone derivs. as cocatalysts for producing optically active aldehyde)

IT 12092-47-6 159398-11-5 179893-92-6 180060-82-6 180060-83-7  
 RL: CAT (Catalyst use); USES (Uses)  
 (prepn. of phosphine compds. as cocatalysts and its complexes as catalysts for producing optically active aldehyde)

IT 14874-82-9, (Acetylacetonato)dicarbonylrhodium  
 RL: CAT (Catalyst use); RCT (Reactant); RACT (Reactant or reagent); USES (Uses)  
 (prepn. of phosphine compds. as cocatalysts and its complexes as catalysts for producing optically active aldehyde)

IT 149917-85-1P 149917-86-2P 149917-87-3P 149952-92-1P 149952-93-2P  
 155566-52-2P 155566-53-3P 155613-50-6P 155613-51-7P 159496-88-5P  
 159496-91-0P 159496-94-3P 159573-28-1P 159573-29-2P 159573-30-5P  
 159573-31-6P 159573-32-7P 159573-33-8P 159573-34-9P  
 RL: CAT (Catalyst use); RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent); USES (Uses)  
 (prepn. of phosphine compds. as cocatalysts and its complexes as catalysts for producing optically active aldehyde)

IT 159398-04-6P 159398-05-7P 159398-06-8P 159398-07-9P 159398-08-0P  
 159398-09-1P 159398-10-4P 159398-23-9P 159398-24-0P 159398-26-2P  
 159436-33-6P 159496-96-5P 159516-49-1P 159516-54-8P 159516-55-9P  
 159516-56-0P 159518-56-6P 179893-91-5P  
 RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation); USES (Uses)  
 (prepn. of phosphine compds. as cocatalysts and its complexes as catalysts for producing optically active aldehyde)

IT 88-04-0, 4-Chloro-3,5-xylenol 95-13-6, 1H-Indene 100-42-5, reactions  
 107-01-7, 2-Butene 108-05-4, Acetic acid ethenyl ester, reactions  
 447-53-0 527-54-8, 3,4,5-Trimethylphenol 592-41-6, 1-Hexene, reactions  
 622-97-9 637-69-4 1073-67-2 3485-84-5 4559-70-0, Diphenylphosphine oxide 5382-00-3, Chlorodiphenoxyphosphine 18531-94-7 18531-99-2, (S)-1,1'-Bi-2-naphthol 63444-56-4 65355-00-2 95033-74-2  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (prepn. of phosphine compds. as cocatalysts and its complexes as catalysts for producing optically active aldehyde)

IT 17763-95-0P 33530-47-1P 34638-21-6P 65355-14-8P 66875-70-5P  
 126613-06-7P 132532-04-8P 137156-22-0P **149917-88-4P**  
**149917-89-5P** 155566-46-4P 155566-47-5P 155566-48-6P  
 155566-49-7P 155566-50-0P 155566-51-1P 155613-52-8P 159496-89-6P  
 159496-90-9P 159496-92-1P 159496-93-2P 159496-95-4P 179893-88-0P  
 179893-89-1P 179893-90-4P  
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)  
 (prepn. of phosphine compds. as cocatalysts and its complexes as catalysts for producing optically active aldehyde)

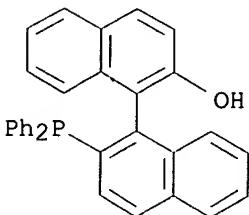
IT 149917-88-4P 149917-89-5P

RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)

(prepn. of phosphine compds. as cocatalysts and its complexes as catalysts for producing optically active aldehyde)

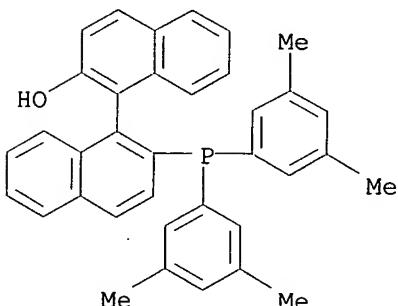
RN 149917-88-4 HCPLUS

CN [1,1'-Binaphthalen]-2-ol, 2'-(diphenylphosphino)-, (1R)- (9CI) (CA INDEX NAME)



RN 149917-89-5 HCPLUS

CN [1,1'-Binaphthalen]-2-ol, 2'-[bis(3,5-dimethylphenyl)phosphino]-, (R)- (9CI) (CA INDEX NAME)



L81 ANSWER 7 OF 18 HCPLUS COPYRIGHT 2003 ACS

AN 1996:169300 HCPLUS

DN 124:343650

TI Optically active tertiary phosphines, their metal complexes, and preparation of optically active organosilicon compounds

IN Iwakura, Kazunori; Minamii, Masayoshi

PA Sumitomo Chemical Co, Japan

SO Jpn. Kokai Tokkyo Koho, 7 pp.

CODEN: JKXXAF

DT Patent

LA Japanese

IC ICM C07F009-50

ICS B01J031-18; C07F007-14; C07F007-18

ICA C07B061-00

ICI C07M007-00

CC 29-6 (Organometallic and Organometalloidal Compounds)  
Section cross-reference(s): 67

FAN.CNT 1

PATENT NO. KIND DATE APPLICATION NO. DATE

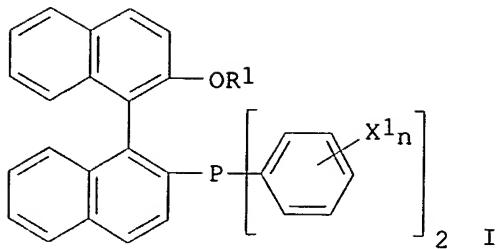
----- ----- ----- ----- -----

PI JP 07330786 A2 19951219 JP 1994-127786 19940609 &lt;--

PRAI JP 1994-127786 19940609 &lt;--

OS CASREACT 124:343650; MARPAT 124:343650

GI



AB The tertiary phosphines I ( $R_1 = H$ , lower alkyl which may be substituted with halo, lower alkoxy, Ph;  $X_1 = \text{halo}$ ;  $n = 1-5$ ) and transition metal complexes having I as the ligands are claimed. Also claimed is a method for the prepn. of optically active  $R_2R_3\text{CHCR}_4R_5\text{Si}X_2X_3X_4$  ( $R_2-5 = \text{alkyl}$ , alkenyl, alkynyl, cycloalkyl, aryl, aralkyl, alkoxy, H; 2 of them may be linked each other to form a ring;  $X_2-4 = H$ , alkyl, alkoxy, halo), useful as synthetic intermediates, by treatment of  $R_2R_3\text{C:CR}_4R_5$  with  $X_2X_3X_4\text{SiH}$  in the presence of transition metal complexes having I as the ligands.  $(4-\text{ClC}_6\text{H}_4)_2\text{P(O)H}$  (prepn. given) was treated with  $(R)-2,2'$ -bis(trifluoromethanesulfonyloxy)-1,1'-binaphthyl (prepn. given) to give  $(R)-2\text{-trifluoromethanesulfonyloxy-2}'\text{-bis(4-chlorophenyl)phosphinoyl-1,1}'\text{-binaphthyl}$ , which was hydrolyzed followed by O-methylation and redn. to give (R)-I ( $R_1 = \text{Me}$ ,  $X_1 = 4\text{-Cl}$ ) (II). A toluene soln. of allylpalladium chloride dimer and II was treated with norbornene and  $\text{SiHCl}_3$  under stirring for 12 h to give 97% (1S,2S,4R)-2-trichlorosilylnorbornane with 95% e.e., vs. 95 and 89% e.e. for a control prepd. using  $(R)-(+)-2\text{-diphenylphosphino-2}'\text{-methoxy-1,1}'\text{-binaphthyl}$  as a ligand.

ST halophenylphosphinobinaphthyl prepn ligand hydrosilylation catalyst; phosphinobinaphthyl halophenylphosphino ligand hydrosilylation catalyst; optically active organosilicon compd prepn

IT Hydrosilylation catalysts  
([bis(halophenyl)phosphino]binaphthyl transition metal complexes)

IT Alkenes, reactions

Cycloalkenes

Silanes

RL: RCT (Reactant); RACT (Reactant or reagent)  
(asym. hydrosilylation of (cyclo)alkenes with silanes using [bis(halophenyl)phosphino]binaphthyl transition metal complexes)

IT 176370-78-8P, (R)-2-Hydroxy-2'-(bis(4-chlorophenyl)phosphino)-1,1'-binaphthyl  
RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation); USES (Uses)  
([bis(halophenyl)phosphino]binaphthyl transition metal complexes as asym. hydrosilylation catalysts)

IT 358-23-6, Trifluoromethanesulfonic anhydride 637-87-6,  
1-Chloro-4-iodobenzene 762-04-9, Diethyl phosphite 122531-87-7,  
(R)-.beta.-Binaphthol  
RL: RCT (Reactant); RACT (Reactant or reagent)  
([bis(halophenyl)phosphino]binaphthyl transition metal complexes as asym. hydrosilylation catalysts)

IT 15948-60-4P, Bis(4-chlorophenyl)phosphine oxide 126613-06-7P,  
(R)-2,2'-Bis(trifluoromethanesulfonyloxy)-1,1'-binaphthyl 176370-75-5P,  
(R)-2-(Trifluoromethanesulfonyloxy)-2'-(bis(4-chlorophenyl)phosphinoyl)-1,1'-binaphthyl 176370-76-6P, (R)-2-Hydroxy-2'-(bis(4-chlorophenyl)phosphinoyl)-1,1'-binaphthyl 176370-77-7P  
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)  
([bis(halophenyl)phosphino]binaphthyl transition metal complexes as asym. hydrosilylation catalysts)

IT 146075-48-1P, (1S,2S,4R)-2-(Trichlorosilyl)norbornane  
 RL: IMF (Industrial manufacture); SPN (Synthetic preparation); PREP (Preparation)  
 (asym. hydrosilylation of (cyclo)alkenes with silanes using [bis(halophenyl)phosphino]binaphthyl transition metal complexes)

IT 498-66-8, Bicyclo[2.2.1]hept-2-ene 10025-78-2  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (asym. hydrosilylation of (cyclo)alkenes with silanes using [bis(halophenyl)phosphino]binaphthyl transition metal complexes)

IT 12012-95-2, Allylpalladium chloride dimer  
 RL: CAT (Catalyst use); USES (Uses)  
 (catalysts contg. (R)-2-methoxy-2'-[bis(4-chlorophenyl)phosphino]-1,1'-binaphthyl; asym. hydrosilylation catalyst)

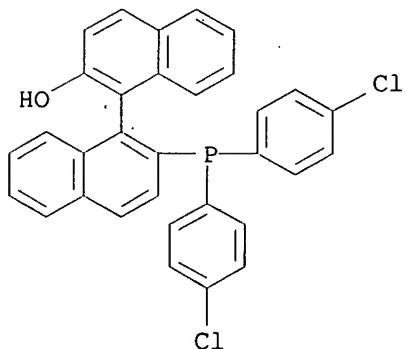
IT 165730-08-5P, (R)-2-Methoxy-2'-[bis(4-chlorophenyl)phosphino]-1,1'-binaphthyl  
 RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation); USES (Uses)  
 (catalysts contg. allylpalladium chloride dimer; [bis(halophenyl)phosphino]binaphthyl transition metal complexes as asym. hydrosilylation catalysts)

IT 61277-93-8P, (1S,2S,4R)-2-Norbornanol  
 RL: SPN (Synthetic preparation); PREP (Preparation)  
 (prepn. of norbornanol from (trichlorosilyl)norbornane)

IT 176370-78-8P, (R)-2-Hydroxy-2'-[bis(4-chlorophenyl)phosphino]-1,1'-binaphthyl  
 RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation); USES (Uses)  
 ([bis(halophenyl)phosphino]binaphthyl transition metal complexes as asym. hydrosilylation catalysts)

RN 176370-78-8 HCPLUS

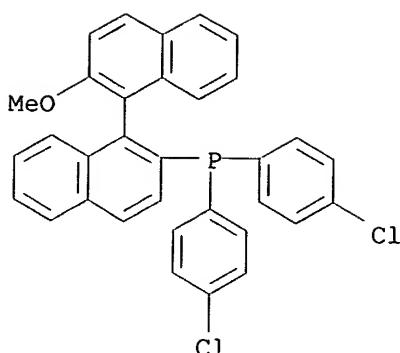
CN [1,1'-Binaphthalen]-2-ol, 2'-[bis(4-chlorophenyl)phosphino]-, (R)- (9CI) (CA INDEX NAME)



IT 165730-08-5P, (R)-2-Methoxy-2'-[bis(4-chlorophenyl)phosphino]-1,1'-binaphthyl  
 RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation); USES (Uses)  
 (catalysts contg. allylpalladium chloride dimer; [bis(halophenyl)phosphino]binaphthyl transition metal complexes as asym. hydrosilylation catalysts)

RN 165730-08-5 HCPLUS

CN Phosphine, bis(4-chlorophenyl)(2'-methoxy[1,1'-binaphthalen]-2-yl)-, (R)- (9CI) (CA INDEX NAME)



L81 ANSWER 8 OF 18 HCAPLUS COPYRIGHT 2003 ACS  
 AN 1996:137584 HCAPLUS  
 DN 124:176140  
 TI Preparation of optically active heteroarylalkanol and arylalkanol  
 IN Azumai, Takayuki; Minamii, Masayoshi; Fujimoto, Yukari; Matsumoto, Tsutomu  
 PA Sumitomo Chemical Co, Japan  
 SO Jpn. Kokai Tokkyo Koho, 14 pp.  
 CODEN: JKXXAF  
 DT Patent  
 LA Japanese  
 IC ICM C07D239-26  
 ICS B01J031-24; C07C029-48; C07C033-24; C07C033-46; C07C041-30;  
 C07C043-23; C07D213-06; C07D213-30; C07D215-20; C07D217-02;  
 C07D237-08; C07D239-34; C07D239-74; C07D239-80; C07D241-12;  
 C07D241-44; C07D401-04; C07D401-10; C07D403-04  
 CC 28-16 (Heterocyclic Compounds (More Than One Hetero Atom))  
 FAN.CNT 1  

| PATENT NO.                                | KIND | DATE         | APPLICATION NO. | DATE         |
|---|------|--------------|-----------------|--------------|
| PI JP 07291940                            | A2   | 19951107     | JP 1994-89663   | 19940427 <-- |
| PRAI JP 1994-89663                        |      | 19940427 <-- |                 |              |
| OS CASREACT 124:176140; MARPAT 124:176140 |      |              |                 |              |

 GI

\* STRUCTURE DIAGRAM TOO LARGE FOR DISPLAY - AVAILABLE VIA OFFLINE PRINT \*

AB The title compd. represented by formula R1(O)<sub>m</sub>A1(A2)pA3(CH<sub>2</sub>)<sub>n</sub>R [I; R = CH(OH)Me; R<sub>1</sub> = C<sub>1</sub>-20 (halo)alkyl, C<sub>2</sub>-20 (halo)alkoxyalkyl; A<sub>1</sub>, A<sub>2</sub>, A<sub>3</sub> = Q - Q<sub>9</sub>; wherein u, w = 0-3; provided that when A<sub>1</sub> = fused ring, A<sub>2</sub> = monocyclic ring or when A<sub>1</sub> = monocyclic ring and p = 1, A<sub>2</sub> and A<sub>3</sub> = monocyclic ring; n = 0-10; m, p = 0,1], useful as an intermediate for agrochems., drugs and ferroelec. liq. crystals, is prep'd. by hydrosilylation of an .alpha.-alkene I (R = CH:CH<sub>2</sub>) with HSi(X<sub>5</sub>)<sub>3</sub> (X<sub>5</sub> = H, alkyl, alkoxy, halo) in the presence of a transition metal complex having an optically active tert-phosphine binaphthyl compd. [R<sub>2</sub> = halo, alkoxy, alkoxyalkoxy, (phenyl)alkyl, C<sub>5</sub>-7 cycloalkyl; R<sub>3</sub> = alkyl, alkoxy, (halo)phenyl; R<sub>4</sub>, R<sub>5</sub> = H, alkyl; or R<sub>4</sub>R<sub>5</sub> forms a fused ring] and oxidn. of the resulting silane I [R = CHMeSi(X<sub>5</sub>)<sub>3</sub>]. Thus, 5.4 g trichlorosilane was slowly added dropwise to a mixt. of 10 g 2-[4-(5-hexen-1-yl)phenyl]-5-octyloxypyrimidine, 0.46 mg .pi.-allylpalladium chloride, and 1.22 mg (S)-I (R<sub>2</sub> = Me, R<sub>3</sub> = Ph, R<sub>4</sub> = R<sub>5</sub> = H) at 25-30.degree. and the resulting mixt. was stirred for 10 h and added to a suspension of 1.7 g KF and 9 g KHCO<sub>3</sub> in 100 mL THF and 100 mL MeOH under ice-cooling. The resulting

mixt. was stirred under ice-cooling for 2 h, followed by adding 25 mL 30% H<sub>2</sub>O<sub>2</sub>, and the reaction mixt. was stirred at 50.degree. for 24 h to give, after silica gel chromatog., the optically active title compd. [(-)-II].

ST heteroarylalkanol optically active prepn; arylalkanol optically active prepn; allylpalladium chloride stereoselective hydrosilylation catalyst; phosphinobinaphthyl hydrosilylation catalyst ligand; trichlorosilane hydrosilylation alkene

IT Hydrosilylation catalysts  
(stereoselective, allylpalladium chloride and phosphinobinaphthyl deriv.; prepn. of optically active heteroarylalkanol and arylalkanol by hydrosilylation of heteroaryl- or aryl-.alpha.-alkene with trichlorosilane)

IT Hydrosilylation  
(stereoselective, prepn. of optically active heteroarylalkanol and arylalkanol by hydrosilylation of heteroaryl- or aryl-.alpha.-alkene with trichlorosilane)

IT 12012-95-2, .pi.-Allylpalladium chloride 134484-36-9  
RL: CAT (Catalyst use); USES (Uses)  
(prepn. of optically active heteroarylalkanol and arylalkanol by hydrosilylation of heteroaryl- or aryl-.alpha.-alkene with trichlorosilane)

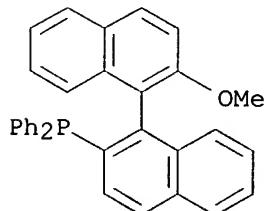
IT 10025-78-2 165320-52-5  
RL: RCT (Reactant); RACT (Reactant or reagent)  
(prepn. of optically active heteroarylalkanol and arylalkanol by hydrosilylation of heteroaryl- or aryl-.alpha.-alkene with trichlorosilane)

IT 174073-63-3P  
RL: SPN (Synthetic preparation); PREP (Preparation)  
(prepn. of optically active heteroarylalkanol and arylalkanol by hydrosilylation of heteroaryl- or aryl-.alpha.-alkene with trichlorosilane)

IT 134484-36-9  
RL: CAT (Catalyst use); USES (Uses)  
(prepn. of optically active heteroarylalkanol and arylalkanol by hydrosilylation of heteroaryl- or aryl-.alpha.-alkene with trichlorosilane)

RN 134484-36-9 HCPLUS

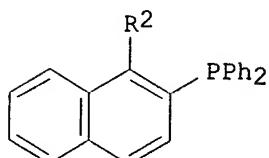
CN Phosphine, [(1S)-2'-methoxy[1,1'-binaphthalen]-2-yl]diphenyl- (9CI) (CA INDEX NAME)



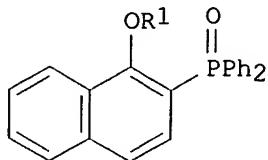
L81 ANSWER 9 OF 18 HCPLUS COPYRIGHT 2003 ACS  
 AN 1995:777644 HCPLUS  
 DN 123:199144  
 TI Preparation of 1-substituted-2-(diphenylphosphino)naphthalenes  
 IN Myano, Sotaro; Hatsutori, Tetsutaro; Sakamoto, Junichi  
 PA Sumitomo Seika Kk, Japan  
 SO Jpn. Kokai Tokkyo Koho, 11 pp.  
 CODEN: JKXXAF  
 DT Patent  
 LA Japanese  
 IC ICM C07F009-50

CC 29-7 (Organometallic and Organometalloidal Compounds)  
 FAN.CNT 1

|      | PATENT NO.                             | KIND | DATE         | APPLICATION NO. | DATE         |
|------|--|------|--------------|-----------------|--------------|
| PI   | JP 06256367                            | A2   | 19940913     | JP 1993-49703   | 19930310 <-- |
| PRAI | JP 1993-49703                          |      | 19930310 <-- |                 |              |
| OS   | CASREACT 123:199144; MARPAT 123:199144 |      |              |                 |              |
| GI   |  |      |              |                 |              |



I



II

AB Title compds. I ( $R_2 = \text{alkyl, aralkyl, aryl, alkoxy, alkylamino}$ ) were prep'd. from 1-alkoxy-2-(oxodiphenylphosphino)naphthalenes II ( $R_1 = \text{alkyl, aralkyl}$ ) by reaction with nucleophiles followed by redn. Thus, reaction of 1-methoxy-2-(oxodiphenylphosphino)naphthalene with NaOMe in DMF gave 78% 1-butoxy-2-(oxodiphenylphosphino)naphthalene, redn of which with HSiCl3 and Et3N in xylene gave 99% 1-butoxy-2-(diphenylphosphino)naphthalene.

ST phosphine triaryl; phenylphosphinonaphthalene; naphthalene diphenylphosphino

IT 90-15-3, 1-Naphthol 109-72-8, reactions 683-60-3, Sodium isopropoxide 693-03-8, n-Butylmagnesium bromide 1079-66-9, Chlorodiphenylphosphine 2372-45-4, Sodium butoxide 4111-54-0, Lithium diisopropylamide 16750-63-3, 2-Methoxyphenylmagnesium bromide 20752-47-0 27303-99-7, (-)-Menthol sodium salt 36321-90-1, 2-Methoxy-1-naphthylmagnesium bromide 167363-32-8

RL: RCT (Reactant); RACT (Reactant or reagent)  
 (prepn. of (diphenylphosphino)naphthalenes)

IT 2216-69-5P, 1-Methoxynaphthalene 161053-37-8P 161053-38-9P  
 161053-42-5P 161053-43-6P 161053-45-8P 161053-51-6P

RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)  
 (prepn. of (diphenylphosphino)naphthalenes)

IT 161053-32-3P 161053-34-5P 161053-39-0P 161053-44-7P  
**161053-46-9P** 161053-47-0P . 161053-48-1P 161053-49-2P  
 167363-33-9P 167363-34-0P

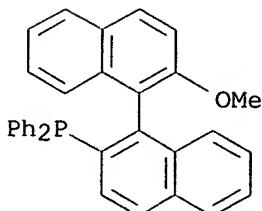
RL: SPN (Synthetic preparation); PREP (Preparation)  
 (prepn. of (diphenylphosphino)naphthalenes)

IT **161053-46-9P**

RL: SPN (Synthetic preparation); PREP (Preparation)  
 (prepn. of (diphenylphosphino)naphthalenes)

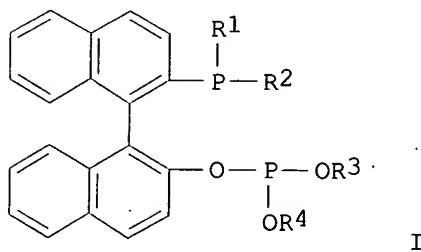
RN 161053-46-9 HCPLUS

CN Phosphine, (2'-methoxy[1,1'-binaphthalen]-2-yl)diphenyl- (9CI) (CA INDEX NAME)



L81 ANSWER 10 OF 18 HCAPLUS COPYRIGHT 2003 ACS  
 AN 1995:742567 HCAPLUS  
 DN 123:198277  
 TI Process and chiral rhodium hydroformylation catalysts for preparing optically active aldehydes.  
 IN Takaya, Hidemasa; Sakai, Nozomu; Tamao, Kyoko Beru; Mano, Satoshi; Kumobayashi, Hidenori; Tomita, Tetsuo  
 PA Mitsubishi Gas Chemical Co., Inc., Japan; Takasago International Corp.  
 SO Eur. Pat. Appl., 12 pp.  
 CODEN: EPXXDW  
 DT Patent  
 LA English  
 IC ICM C07C045-50  
 ICS C07C045-49; C07C047-14; C07C047-228; C07C047-277; C07C067-293;  
 C07C069-14; C07D209-48; C07C253-30; C07C255-17  
 CC 23-14 (Aliphatic Compounds)  
 Section cross-reference(s): 67  
 FAN.CNT .5

|      | PATENT NO.                             | KIND | DATE         | APPLICATION NO. | DATE         |
|------|--|------|--------------|-----------------|--------------|
| PI   | EP 614870                              | A2   | 19940914     | EP 1994-103675  | 19940310 <-- |
|      | EP 614870                              | A3   | 19941109     |                 |              |
|      | EP 614870                              | B1   | 19980114     |                 |              |
|      | R: DE, FR, GB                          |      |              |                 |              |
|      | JP 06263681                            | A2   | 19940920     | JP 1993-52539   | 19930312 <-- |
| PRAI | JP 1993-52539                          | A    | 19930312 <-- |                 |              |
| OS   | CASREACT 123:198277; MARPAT 123:198277 |      |              |                 |              |
| GI   |  |      |              |                 |              |



AB Optically active aldehydes  $\text{OHCCH}(\text{CH}_3)\text{Q}$  [ $\text{Q}$  = halogen, lower alkyl, phthalimido, lower alkylcarbonyloxy, CN, (un)substituted Ph, etc.] [e.g., (S)-2-phenylpropanal], which are expensively synthesized using prior-art techniques, can be produced in high yield and at low cost by hydroformylating an olefin  $\text{H}_2\text{C}:\text{CHQ}$  (e.g., vinyl acetate) in the presence of a rhodium catalyst system contg. a chiral phosphine ligand [I; R1, R2 = (un)substituted Ph; R3, R4 = lower alkyl, (un)substituted Ph].  
 ST catalyst rhodium asym hydroformylation; chiral aldehyde prepn asym hydroformylation alkene  
 IT Hydroformylation catalysts  
 (asym., chiral rhodium complexes for prep. optically active aldehydes)  
 IT Aldehydes, preparation  
 RL: SPN (Synthetic preparation); PREP (Preparation)  
 (chiral, process and chiral rhodium hydroformylation catalysts for prep.)  
 IT Hydroformylation  
 (stereoselective, prep. optically active aldehydes by)  
 IT 4559-70-0, Diphenylphosphine oxide 6737-42-4, 1,3-Bis(diphenylphosphino)propane 14874-82-9 18531-94-7,

(R)-1,1'-Bi-2-naphthol 18531-99-2, (S)-1,1'-Bi-2-naphthol 155613-52-8  
 RL: CAT (Catalyst use); RCT (Reactant); RACT (Reactant or reagent); USES (Uses)  
 (catalyst precursor; process and chiral rhodium hydroformylation catalysts for prep. optically active aldehydes)

IT 126613-06-7P 132532-04-8P 137156-22-0P 149917-85-1P  
**149917-88-4P** 149952-92-1P  
 RL: CAT (Catalyst use); RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent); USES (Uses)  
 (catalyst precursor; process and chiral rhodium hydroformylation catalysts for prep. optically active aldehydes)

IT 104-53-0P, 3-Phenylpropanal 18545-28-3P, 3-Acetoxypropanal  
 RL: BYP (Byproduct); PREP (Preparation)  
 (process and chiral rhodium hydroformylation catalysts for prep. optically active aldehydes)

IT 159516-56-0  
 RL: CAT (Catalyst use); USES (Uses)  
 (process and chiral rhodium hydroformylation catalysts for prep. optically active aldehydes)

IT 75-01-4, Vinyl chloride, reactions 100-42-5, Styrene, reactions 107-13-1, Acrylonitrile, reactions 108-05-4, Vinyl acetate, reactions 622-97-9, 4-Methylstyrene 630-08-0, Carbon monoxide, reactions 637-69-4, 4-Methoxystyrene 1073-67-2, 4-Chlorostyrene 26206-42-8, 4-Butylstyrene 63444-51-9, 2-Methoxy-6-vinylnaphthalene 63444-56-4, 4-Isobutylstyrene 84494-80-4  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (process and chiral rhodium hydroformylation catalysts for prep. optically active aldehydes)

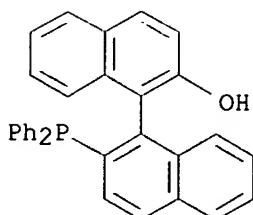
IT 33530-47-1P, (S)-2-Phenylpropanal 66875-70-5P  
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)  
 (process and chiral rhodium hydroformylation catalysts for prep. optically active aldehydes)

IT 111-71-7P, Heptanal 5406-12-2P 6034-46-4P 7782-24-3P,  
 (S)-(+)-2-Phenylpropionic acid 20401-88-1P 40764-03-2P 75677-02-0P  
 110773-62-1P 122091-55-8P 132151-88-3P 147922-82-5P 149917-84-0P  
 166587-68-4P 166587-69-5P  
 RL: SPN (Synthetic preparation); PREP (Preparation)  
 (process and chiral rhodium hydroformylation catalysts for prep. optically active aldehydes)

IT **149917-88-4P**  
 RL: CAT (Catalyst use); RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent); USES (Uses)  
 (catalyst precursor; process and chiral rhodium hydroformylation catalysts for prep. optically active aldehydes)

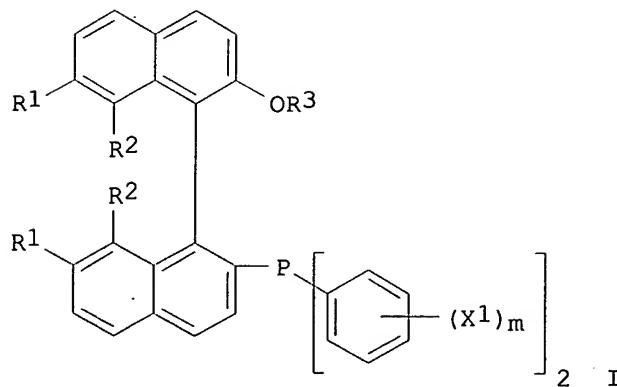
RN 149917-88-4 HCPLUS

CN [1,1'-Binaphthalen]-2-ol, 2'-(diphenylphosphino)-, (1R)- (9CI) (CA INDEX NAME)



DN 123:144274  
 TI Preparation of tertiary phosphines and their transition metal complexes as catalysts for asymmetric synthesis reactions  
 IN Hayashi, Tamio; Uozumi, Yasuhiro; Iwakura, Kazunori; Kurimoto, Isao; Minai, Masayoshi  
 PA Sumitomo Chemical Co., Ltd., Japan  
 SO Eur. Pat. Appl., 21 pp.  
 CODEN: EPXXDW  
 DT Patent  
 LA English  
 IC ICM C07F009-50  
 ICS B01J031-28; C07F015-00; C07F007-08; C07F007-14; C07F007-18; C07C001-22  
 ICI C07M005-00, C07M007-00  
 CC 29-7 (Organometallic and Organometalloidal Compounds)  
 Section cross-reference(s): 21  
 FAN.CNT 1  

|      | PATENT NO.            | KIND | DATE         | APPLICATION NO. | DATE         |
|------|-----------------------|------|--------------|-----------------|--------------|
| PI   | EP 647647             | A1   | 19950412     | EP 1994-111780  | 19940728 <-- |
|      | EP 647647             | B1   | 20011024     |                 |              |
|      | R: CH, DE, FR, GB, LI |      |              |                 |              |
|      | JP 07149776           | A2   | 19950613     | JP 1994-15341   | 19940209 <-- |
|      | JP 07224073           | A2   | 19950822     | JP 1994-16760   | 19940210 <-- |
|      | US 5523437            | A    | 19960604     | US 1994-280814  | 19940726 <-- |
| PRAI | JP 1993-251635        | A    | 19931007 <-- |                 |              |
|      | JP 1994-15341         | A    | 19940209 <-- |                 |              |
|      | JP 1994-16760         | A    | 19940210 <-- |                 |              |
| OS   | MARPAT 123:144274     |      |              |                 |              |
| GI   |                       |      |              |                 |              |



AB The prepn. of tertiary phosphine compd. I (R1, R2 = independently from each other a H, Me; R1R2 = CH:CHCH:CH; R3 = H, C5-7 cycloalkyl, lower alkyl group which may be substituted with halogen, lower alkoxy, lower alkoxyalkoxy, Ph; X1 = halogen atom when both R1 and R2 are hydrogens, hydrogen atom, halogen atom, lower alkyl group, lower alkoxy group when at least one of R1 and R2 is not a hydrogen atoms; m = 1-5), useful as ligand of a transition metal complex that can catalyze various reactions, is described. Thus, redn. of (R)-(+)-3-diphenylphosphinyl-3'-methoxy-4,4'-biphenanthryl (prepn. given) with HSiCl3 in the presence of Et3N gave title compd., (R)-(+)-3-diphenylphosphino-3'-methoxy-4,4'-biphenanthryl (II), which was used in asym. synthesis of .alpha.-olefins. Thus, tris(dibenzylideneacetone)(chloroform)dipalladium(0)-catalyzed reaction of

geranyl methyl carbonate with formic acid in the presence of 1,8-bis(dimethylamino)naphthalene and chiral cocatalyst II gave (S)-3,7-dimethyl-1,6-octadiene.

ST tertiary phosphine prepn cocatalyst asym synthesis; biphenanthryl phosphine prepn cocatalyst asym synthesis; palladium phosphine complex catalyst asym synthesis

IT Catalysts and Catalysis  
 (asym. synthesis; prepn. of tertiary phosphines and their transition metal complexes as catalysts for asym. synthesis reactions)

IT Asymmetric synthesis and induction  
 (prepn. of tertiary phosphines and their transition metal complexes as catalysts for asym. synthesis reactions)

IT 26593-50-0, 2-Hydroxy-7-methylnaphthalene  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (oxidn. of)

IT 4559-70-0, Diphenylphosphine oxide  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (phosphonylation of trifloxybiphenanthryl with)

IT 1115-82-8P  
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)  
 (prepn. and anilide formation of)

IT 103981-06-2P, (S)-3-Triethylsilyl-1-butene  
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)  
 (prepn. and carbamylation of)

IT 157397-73-4P 165730-04-1P  
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)  
 (prepn. and hydrolysis of)

IT 157397-74-5P 165730-05-2P  
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)  
 (prepn. and methylation of)

IT 10281-55-7P, (S)-3,7-Dimethyl-1,6-octadiene 146075-48-1P  
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)  
 (prepn. and oxidn. of)

IT 18531-94-7P 157397-72-3P 165730-03-0P  
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)  
 (prepn. and phosphorylation of)

IT 157397-75-6P 165730-06-3P  
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)  
 (prepn. and redn. of)

IT 157584-78-6P  
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)  
 (prepn. and resoln. of)

IT 100838-76-4P, (R)-(-)-3,3'-Dihydroxy-4,4'-biphenanthryl 157584-79-7P,  
 (R)-(+)-2,2'-Dihydroxy-7,7'-dimethyl-1,1'-binaphthyl  
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)  
 (prepn. and triflation of)

IT 10281-56-8P, (R)-3,7-Dimethyl-1,6-octadiene 36617-88-6P 61277-93-8P  
 84170-98-9P 100838-77-5P, (S)-(+)-3,3'-Dihydroxy-4,4'-biphenanthryl  
 125847-56-5P, (R)-3-Cyclohexyl-1-butene 153279-32-4P 157397-77-8P  
 157397-78-9P 157584-80-0P, (S)-(-)-2,2'-Dihydroxy-7,7'-dimethyl-1,1'-binaphthyl 161550-38-5P  
 RL: SPN (Synthetic preparation); PREP (Preparation)  
 (prepn. of)

IT 6737-42-4 12012-95-2 51364-51-3

RL: CAT (Catalyst use); USES (Uses)  
 (prepn. of tertiary phosphines and their transition metal complexes as catalysts for asym. synthesis reactions)

IT 155184-93-3P **165730-07-4P 165730-08-5P**  
 RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation); USES (Uses)  
 (prepn. of tertiary phosphines and their transition metal complexes as catalysts for asym. synthesis reactions)

IT 20734-58-1, 1,8-Bis(dimethylamino)naphthalene  
 RL: NUU (Other use, unclassified); USES (Uses)  
 (prepn. of tertiary phosphines and their transition metal complexes as catalysts for asym. synthesis reactions)

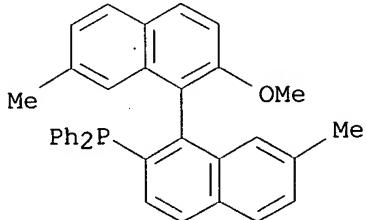
IT 498-66-8, Bicyclo[2.2.1]hept-2-ene 630-19-3, Pivalic aldehyde  
 85217-72-7, Geranyl methyl carbonate 85217-73-8 155184-90-0  
 157397-76-7 158261-40-6 158261-41-7  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (prepn. of tertiary phosphines and their transition metal complexes as catalysts for asym. synthesis reactions)

IT 158261-46-2P, (R)-3-Phenyl-3-triethylsilyl-1-propene  
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Réactant or reagent)  
 (prepn. of tertiary phosphines and their transition metal complexes as catalysts for asym. synthesis reactions)

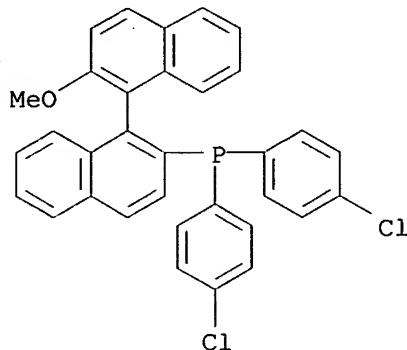
IT 100780-04-9  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (resoln. of)

IT **165730-07-4P 165730-08-5P**  
 RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation); USES (Uses)  
 (prepn. of tertiary phosphines and their transition metal complexes as catalysts for asym. synthesis reactions)

RN 165730-07-4 HCPLUS  
 CN Phosphine, (2'-methoxy-7,7'-dimethyl[1,1'-binaphthalen]-2-yl)diphenyl-,  
 (R)- (9CI) (CA INDEX NAME)



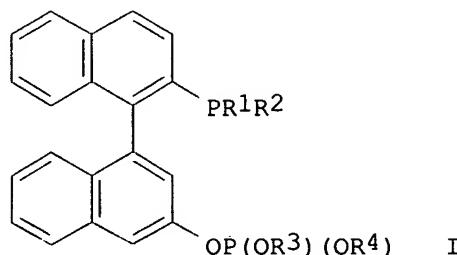
RN 165730-08-5 HCPLUS  
 CN Phosphine, bis(4-chlorophenyl)(2'-methoxy[1,1'-binaphthalen]-2-yl)-, (R)- (9CI) (CA INDEX NAME)



L81 ANSWER 12 OF 18 HCPLUS COPYRIGHT 2003 ACS  
 AN 1995:231203 HCPLUS  
 DN 122:10257  
 TI preparation of phosphine compounds and their transition metal complexes  
 IN Takaya, Hidemasa; Sakai, Nozomu; Tamao, Kyoko Beru Mezon; Mano, Satoshi;  
 Kumabayashi, Hidenor; Tomita, Tetsu  
 PA Mitsubishi Gas Chemical Company, Inc., Japan; Takasago International  
 Corporation  
 SO Eur. Pat. Appl., 12 pp.  
 CODEN: EPXXDW  
 DT Patent  
 LA English  
 IC ICM C07F009-50  
 ICS C07F015-00; C07C045-50; C07F009-6574; C07F009-6568  
 CC 29-7 (Organometallic and Organometalloidal Compounds)  
 Section cross-reference(s): 67, 78

FAN.CNT 5

|      | PATENT NO.                           | KIND | DATE         | APPLICATION NO. | DATE         |
|------|--------------------------------------|------|--------------|-----------------|--------------|
| PI   | EP 614901                            | A1   | 19940914     | EP 1994-103674  | 19940310 <-- |
|      | EP 614901                            | B1   | 19980812     |                 |              |
|      | R: CH, DE, FR, GB, IT, LI, NL        |      |              |                 |              |
|      | JP 06263776                          | A2   | 19940920     | JP 1993-52538   | 19930312 <-- |
|      | JP 3313805                           | B2   | 20020812     |                 |              |
| PRAI | JP 1993-52538                        | A    | 19930312 <-- |                 |              |
| OS   | CASREACT 122:10257; MARPAT 122:10257 |      |              |                 |              |
| GI   |                                      |      |              |                 |              |



AB Disclosed herein is the prepn. of phosphine compd. I (R<sub>1</sub>, R<sub>2</sub> = same or different halo or lower alkyl group substituted Ph, divalent hydrocarbon group; R<sub>3</sub>, R<sub>4</sub> = same or different alkyl, halo or lower alkyl group substituted Ph, divalent hydrocarbon group), and their transition metal-phosphine complexes. When the transition metal-phosphine complex is

used as a catalyst for asym. synthesis, an intended product having a desired abs. configuration can be obtained in a high optical purity at a high yield. Thus, reaction of (R)-2-diphenylphosphino-2'-hydroxy-1,1'-binaphthyl (prepn. given) with (S)-1,1'-binaphthalene-2,2'-diyldioxychlorophosphine (prepn. given) in the presence of Et<sub>3</sub>N in Et<sub>2</sub>O gave 98% title phosphine, (R)-2-diphenylphosphino-1,1'-binaphthalene-2'-yloxy((S)-1,1'-binaphthalene-2,2'-diyldioxy)phosphine, which was reacted with [Rh(CO)<sub>2</sub>(acac)] to give asym. hydroformylation catalyst for vinyl acetate or styrene.

ST diphosphine prep transition metal ligand; rhodium diphosphine complex  
prep hydroformylation catalyst

IT Hydroformylation catalysts  
(asym., prepn. of phosphine compds. and their transition metal complexes)

IT 104-53-0P, Benzenepropanal 18545-28-3P 33530-47-1P 66875-70-5P  
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)  
(prepn. and oxidn. of)

IT 6034-46-4P 7782-24-3P  
RL: SPN (Synthetic preparation); PREP (Preparation)  
(prepn. of)

IT 100-42-5, reactions 108-05-4, Acetic acid ethenyl ester, reactions  
RL: RCT (Reactant); RACT (Reactant or reagent)  
(prepn. of diphosphine rhodium complex for hydrhydroformylation of)

IT 159398-08-0P 159398-09-1P 159398-10-4P 159516-56-0P  
RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation); USES (Uses)  
(prepn. of phosphine compds. and their transition metal complexes)

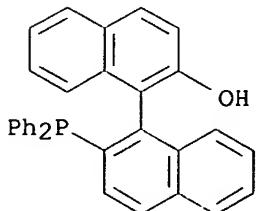
IT 108-48-5, 2,6-Lutidine 4559-70-0, Diphenylphosphine oxide 5382-00-3,  
Chlorodiphenoxypyrophosphine 6737-42-4, 1,3-Bis(diphenylphosphino)propane  
7719-12-2, Phosphorus trichloride 14874-82-9,  
(Acetylacetato)dicarbonylrhodium 18531-94-7, (R)-1,1'-Bi-2-naphthol  
18531-99-2, (S)-1,1'-Bi-2-naphthol  
RL: RCT (Reactant); RACT (Reactant or reagent)  
(prepn. of phosphine compds. and their transition metal complexes)

IT 126613-06-7P 132532-04-8P 137156-22-0P 149917-85-1P 149917-86-2P  
149917-87-3P 149917-88-4P 149917-89-5P 149952-92-1P  
155613-52-8P  
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)  
(prepn. of phosphine compds. and their transition metal complexes)

IT 149917-88-4P 149917-89-5P  
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)  
(prepn. of phosphine compds. and their transition metal complexes)

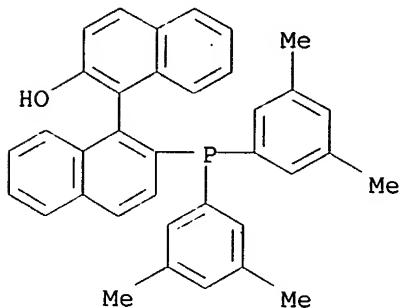
RN 149917-88-4 HCPLUS

CN [1,1'-Binaphthalen]-2-ol, 2'-(diphenylphosphino)-, (1R)- (9CI) (CA INDEX NAME)



RN 149917-89-5 HCPLUS

CN [1,1'-Binaphthalen]-2-ol, 2'-[bis(3,5-dimethylphenyl)phosphino]-, (R)- (9CI) (CA INDEX NAME)



L81 ANSWER 13 OF 18 HCAPLUS COPYRIGHT 2003 ACS  
 AN 1995:231201 HCAPLUS

DN 122:239952

TI Preparation of diphosphines and rhodium complexes and their use for producing optically active aldehydes and 4-[*(R*)-1'-formylethyl]azetidin-2-one derivatives.

IN Saito, Takao; Matsumura, Kazuhiko; Kato, Yasushi; Sayo, Noboru; Kumobayashi, Hidenori

PA Takasago International Corporation, Japan

SO Eur. Pat. Appl., 31 pp.  
CODEN: EPXXDW

DT Patent

LA English

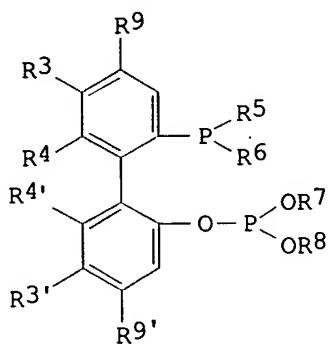
IC ICM C07F009-50

ICS C07F015-00; C07C045-50; C07F009-6574; C07F009-6568; C07D205-08

CC 29-7 (Organometallic and Organometalloidal Compounds)  
Section cross-reference(s): 26, 67, 78

FAN.CNT 5

|      | PATENT NO.                             | KIND | DATE         | APPLICATION NO. | DATE         |
|------|--|------|--------------|-----------------|--------------|
| PI   | EP 614903                              | A2   | 19940914     | EP 1994-301775  | 19940311 <-- |
|      | EP 614903                              | A3   | 19950111     |                 |              |
|      | EP 614903                              | B1   | 20000920     |                 |              |
|      | R: CH, DE, FR, GB, IT, LI, NL          |      |              |                 |              |
|      | JP 06316560                            | A2   | 19941115     | JP 1994-54426   | 19940301 <-- |
|      | JP 3277065                             | B2   | 20020422     |                 |              |
|      | JP 2002128759                          | A2   | 20020509     | JP 2001-328632  | 19940301 <-- |
|      | EP 684249                              | A1   | 19951129     | EP 1995-111575  | 19940311 <-- |
|      | EP 684249                              | B1   | 20030219     |                 |              |
|      | R: CH, DE, FR, GB, IT, LI, NL          |      |              |                 |              |
|      | EP 684230                              | A1   | 19951129     | EP 1995-111576  | 19940311 <-- |
|      | EP 684230                              | B1   | 20020703     |                 |              |
|      | R: CH, DE, FR, GB, IT, LI, NL          |      |              |                 |              |
| PRAI | JP 1993-77484                          | A    | 19930312 <-- |                 |              |
|      | JP 1994-54426                          | A3   | 19940301 <-- |                 |              |
|      | EP 1994-301775                         | A3   | 19940311 <-- |                 |              |
| OS   | CASREACT 122:239952; MARPAT 122:239952 |      |              |                 |              |
| GI   |  |      |              |                 |              |



AB The prepn. of novel phosphine compds., e.g. I ( $R_4, R_4' = H$ , lower alkyl, alkoxy;  $R_3, R_3', R_9, R_9' = H$ , lower alkyl, alkoxy, halo;  $R_3R_4, R_3'R_4' =$  ring;  $R_5, R_6 =$  (un)substituted Ph, halo, lower alkoxy;  $R_7, R_8 =$  (un)substituted Ph;  $R_7R_8 =$  divalent hydrocarbon), useful in the form of their transition metal complexes, or or compds. with transition metals, in producing an optically active aldehyde by hydroformylation of an olefin with high positional and steric selectivities, are described.

4-[ $(R)$ -1'-formylethyl]azetidin-2-one derivs. obtainable by the process is particularly useful as an intermediate for the prepn. of carbapenem antibiotics. Thus, reaction of (+)-3,3'-dichloro-2,2',4,4'-tetramethyl-6-diphenylphosphino-6'-hydroxybiphenyl (prepn. given) with ( $R$ )-1,1'-binaphthalene-2,2'-diyldioxychlorophosphine (prepn. given) in PhMe in the presence of Et<sub>3</sub>N gave (S)-3,3'-dichloro-2,2',4,4'-tetramethyl-6-diphenylphosphinobiphenyl-6'-yloxy( $(R)$ -1,1'-binaphthalene-2,2'-diyldioxy)phosphine (II). Hydroformylation of styrene in the presence of Rh(acac)(CO)<sub>2</sub> (catalyst) and ligand II gave good yield of (S)-(+)-2-phenylpropanal with 94% enantiomeric excess.

ST diphosphine ligand prep catalyst hydroformylation; rhodium diphosphine complex prep hydroformylation catalyst; aldehyde optically active prep; azetidinone hydroformylation catalyst; formylethylazetidinone optically active prep

IT Stereochemistry  
(of hydroformylation of olefins and azetidinones)

IT Hydroformylation  
(of olefins and azetidinones)

IT Hydroformylation catalysts  
(prep. of diphosphines and rhodium complexes and their use for producing optically active aldehydes and formylethylazetidinone derivs.)

IT Alkenes, reactions  
RL: RCT (Reactant); RACT (Reactant or reagent)  
(prep. of diphosphines and rhodium complexes and their use for producing optically active aldehydes and formylethylazetidinone derivs.)

IT Aldehydes, preparation  
RL: SPN (Synthetic preparation); PREP (Preparation)  
(prep. of diphosphines and rhodium complexes and their use for producing optically active aldehydes and formylethylazetidinone derivs.)

IT 95-13-6, 1H-Indene 100-42-5, Styrene, reactions 107-01-7, 2-Butene 108-05-4, Vinyl acetate, reactions 447-53-0 592-41-6, 1-Hexene, reactions 112256-72-1  
RL: RCT (Reactant); RACT (Reactant or reagent)  
(hydroformylation; prep. of diphosphines and rhodium complexes and their use for producing optically active aldehydes and formylethylazetidinone derivs.)

IT 3375-31-3, Palladium acetate 12092-47-6 149952-93-2 159398-11-5

159496-99-8  
 RL: CAT (Catalyst use); USES (Uses)  
 (prepn. of diphosphines and rhodium complexes and their use for  
 producing optically active aldehydes and formylethylazetidinone  
 derivs.)

IT 31096-69-2  
 RL: CAT (Catalyst use); RCT (Reactant); RACT (Reactant or reagent); USES  
 (Uses)  
 (prepn. of diphosphines and rhodium complexes and their use for  
 producing optically active aldehydes and formylethylazetidinone  
 derivs.)

IT 149917-85-1P 149917-86-2P 149917-87-3P 149952-92-1P 155566-52-2P  
 155566-53-3P 155613-50-6P 155613-51-7P 159496-88-5P 159496-92-1P  
 159496-94-3P 159496-96-5P 159573-28-1P 159573-29-2P 159573-30-5P  
 159573-31-6P 159573-32-7P 159573-33-8P 159573-34-9P  
 RL: CAT (Catalyst use); RCT (Reactant); SPN (Synthetic preparation); PREP  
 (Preparation); RACT (Reactant or reagent); USES (Uses)  
 (prepn. of diphosphines and rhodium complexes and their use for  
 producing optically active aldehydes and formylethylazetidinone  
 derivs.)

IT 159398-04-6P 159398-05-7P 159398-06-8P 159398-07-9P 159398-08-0P  
 159398-09-1P 159398-10-4P 159516-49-1P 159516-56-0P 159518-56-6P  
 RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation);  
 USES (Uses)  
 (prepn. of diphosphines and rhodium complexes and their use for  
 producing optically active aldehydes and formylethylazetidinone  
 derivs.)

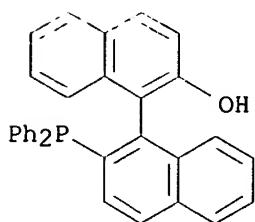
IT 88-04-0, 4-Chloro-3,5-xylenol 527-54-8, 3,4,5-Trimethylphenol  
 4559-70-0, Diphenylphosphine oxide 7719-12-2, Phosphorus trichloride  
 18531-94-7, (R)-1,1'-Bi-2-naphthol 18531-99-2, (S)-1,1'-Bi-2-naphthol  
 65355-00-2  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (prepn. of diphosphines and rhodium complexes and their use for  
 producing optically active aldehydes and formylethylazetidinone  
 derivs.)

IT 17763-95-0P 65355-14-8P 126613-06-7P 132532-04-8P 137156-22-0P  
**149917-88-4P** 155566-49-7P 155566-51-1P 155613-52-8P  
 159496-80-7P 159496-81-8P 159496-82-9P 159496-83-0P 159496-84-1P  
 159496-85-2P 159496-86-3P 159496-87-4P 159496-89-6P 159496-90-9P  
 159496-91-0P 159496-93-2P 159496-95-4P  
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT  
 (Reactant or reagent)  
 (prepn. of diphosphines and rhodium complexes and their use for  
 producing optically active aldehydes and formylethylazetidinone  
 derivs.)

IT 33204-48-7P 33530-47-1P 38235-74-4P 66875-69-2P 66875-70-5P  
 66875-71-6P 155566-54-4P 159496-97-6P 159496-98-7P 159573-35-0P  
 RL: SPN (Synthetic preparation); PREP (Preparation)  
 (prepn. of diphosphines and rhodium complexes and their use for  
 producing optically active aldehydes and formylethylazetidinone  
 derivs.)

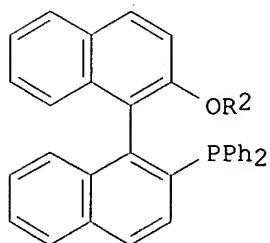
IT **149917-88-4P**  
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT  
 (Reactant or reagent)  
 (prepn. of diphosphines and rhodium complexes and their use for  
 producing optically active aldehydes and formylethylazetidinone  
 derivs.)

RN 149917-88-4 HCPLUS  
 CN [1,1'-Binaphthalen]-2-ol, 2'-(diphenylphosphino)-, (1R)- (9CI) (CA INDEX  
 NAME)



L81 ANSWER 14 OF 18 HCPLUS COPYRIGHT 2003 ACS  
 AN 1995:128170 HCPLUS  
 DN 122:81619  
 TI Preparation of optically active trichlorosilanes  
 IN Hayashi, Tamio; Uozumi, Yasuhiro; Tanahashi, Asako  
 PA Takasago Perfumery Co Ltd, Japan  
 SO Jpn. Kokai Tokkyo Koho, 6 pp.  
 CODEN: JKXXAF  
 DT Patent  
 LA Japanese  
 IC ICM C07F007-12  
 ICS B01J027-18; C07B053-00  
 ICA C07B061-00  
 CC 29-6 (Organometallic and Organometalloidal Compounds)  
 FAN.CNT 1

|      | PATENT NO.                           | KIND     | DATE                 | APPLICATION NO. | DATE         |
|------|--------------------------------------|----------|----------------------|-----------------|--------------|
| PI   | JP 06199875<br>JP 2908919            | A2<br>B2 | 19940719<br>19990623 | JP 1991-292676  | 19911004 <-- |
| PRAI | JP 1991-292676                       |          | 19911004 <--         |                 |              |
| OS   | CASREACT 122:81619; MARPAT 122:81619 |          |                      |                 |              |
| GI   |                                      |          |                      |                 |              |



I

AB Optically active MeCR<sub>1</sub>SiCl<sub>3</sub> (I; R<sub>1</sub> = C<sub>2</sub>-10 alkyl) are prep'd. by asym. hydrosilylation of CH<sub>2</sub>:CHR<sub>1</sub> (II; R<sub>1</sub> = same as I) by HSiCl<sub>3</sub> in presence of optically active phosphines III [R<sub>2</sub> = H, C<sub>5</sub>-7 cycloalkyl, (halo-, lower alkoxy-, or Ph-substituted) C<sub>1</sub>-6 alkyl] and Pd complexes. A mixt. of 1-octene, HSiCl<sub>3</sub>, [(*.pi.*-allyl)PdCl]<sub>2</sub>, and (S)-(-)-III (R<sub>2</sub> = Me) was stirred at 40.degree. for 72 h to give 83% optically active 2-trichlorosilyloctane.  
 ST chlorosilane optically active prep'n; silane trichloro optically active prep'n; alkene asym hydrosilylation trichlorosilane catalyst; phosphine alkene asym hydrosilylation trichlorosilane; palladium alkene asym hydrosilylation trichlorosilane  
 IT Stereochemistry  
 (prep'n. of optically active trichlorosilanes by asym. hydrosilylation of trichlorosilane to alkenes with phosphines and Pd complexes)  
 IT Hydrosilylation

## Hydrosilylation catalysts

(stereoselective, prepn. of optically active trichlorosilanes by asym.  
hydrosilylation of trichlorosilane to alkenes with phosphines and Pd  
complexes)

IT 12012-95-2

RL: CAT (Catalyst use); USES (Uses)  
(catalyst; prepn. of optically active trichlorosilanes by asym.  
hydrosilylation of trichlorosilane to alkenes with phosphines and Pd  
complexes)

IT 134484-36-9P

RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation);  
USES (Uses)  
(catalyst; prepn. of optically active trichlorosilanes by asym.  
hydrosilylation of trichlorosilane to alkenes with phosphines and Pd  
complexes)

IT 18225-07-5P

RL: SPN (Synthetic preparation); PREP (Preparation)  
(optically active; prepn. of optically active trichlorosilanes by asym.  
hydrosilylation of trichlorosilane to alkenes with phosphines and Pd  
complexes)

IT 4559-70-0, Diphenylphosphine oxide 18531-99-2

RL: RCT (Reactant); RACT (Reactant or reagent)  
(prepn. of optically active phosphine catalyst from binaphthol)

IT 128544-05-8P 134484-37-0P 137769-33-6P 137769-34-7P

RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT  
(Reactant or reagent)  
(prepn. of optically active phosphine catalyst from binaphthol)

IT 111-66-0, 1-Octene 10025-78-2, Trichlorosilane

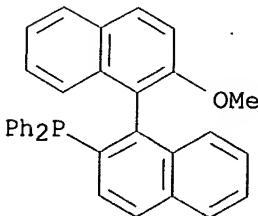
RL: RCT (Reactant); RACT (Reactant or reagent)  
(prepn. of optically active trichlorosilanes by asym. hydrosilylation  
of trichlorosilane to alkenes with phosphines and Pd complexes)

IT 134484-36-9P

RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation);  
USES (Uses)  
(catalyst; prepn. of optically active trichlorosilanes by asym.  
hydrosilylation of trichlorosilane to alkenes with phosphines and Pd  
complexes)

RN 134484-36-9 HCPLUS

CN Phosphine, [(1S)-2'-methoxy[1,1'-binaphthalen]-2-yl]diphenyl- (9CI) (CA  
INDEX NAME)



L81 ANSWER 15 OF 18 HCPLUS COPYRIGHT 2003 ACS

AN 1994:218162 HCPLUS

DN 120:218162

TI Optically active allylfluorosilanes and their preparation

IN Hyama, Tamejiro; Hatanaka, Yasuo

PA Sagami Chem Res, Japan

SO Jpn. Kokai Tokkyo Koho, 8 pp.

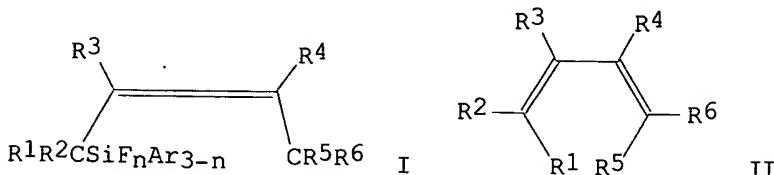
CODEN: JKXXAF

DT Patent

LA Japanese

IC ICM C07F007-12  
 ICS B01J031-22; B01J031-24  
 ICA C07B061-00  
 CC 29-6 (Organometallic and Organometalloidal Compounds)  
 FAN.CNT 1

|      | PATENT NO.                             | KIND | DATE     | APPLICATION NO. | DATE         |
|------|--|------|----------|-----------------|--------------|
| PI   | JP 05255353                            | A2   | 19931005 | JP 1992-88376   | 19920313 <-- |
| PRAI | JP 1992-88376                          |      | 19920313 | <--             |              |
| OS   | CASREACT 120:218162; MARPAT 120:218162 |      |          |                 |              |
| GI   |  |      |          |                 |              |



AB The title compds. I (R1 - R6 = H, alkyl, aryl, silyl; R1 = R2 . noteq. H; Ar = aryl; R1R2, R2R3, R3R4, R4R5, R5R6, R1R6 may be bonded to form a ring; n = 1, 2, 3), useful as intermediates for optically active allyl alcs., are prep'd. by treating butadienes II with HSiFnAr3-n in the presence of group 10 transition metal complex catalysts with optically active ligands. (E)-PhCH:CHCH:CH2 was treated with HSiPhF2 in the presence of PdCl2L [L = (R)-N,N-dimethyl-1-(S)-2-(diphenylphosphinoferrocenyl)ethylamine] at room temp. for 22 h to give 53% (S)-(Z)-PhCH(SiF2Ph)CH:CHMe of 99% e.e.

ST allylfluorosilane chiral prepn; fluoroallylsilane optically active prepn; hydrosilane reaction butadiene; hydrosilylation asym butadiene; group 10 catalyst hydrosilylation butadiene; allyl alc chiral intermediate allylsilane

IT Asymmetric synthesis and induction  
 (of allylfluorosilanes, by group 10 metal-catalyzed hydrosilylation of butadienes)

IT Alcohols, preparation  
 RL: SPN (Synthetic preparation); PREP (Preparation)  
 (allyl, prepn. of, optically active fluoroallylsilanes as intermediates for)

IT Group VIII element compounds  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (complexes, chiral, catalysts, for asym. hydrosilylation of butadienes)

IT Silanes  
 RL: SPN (Synthetic preparation); PREP (Preparation)  
 (fluoro, allyl, chiral, prepn. of, by asym. hydrosilylation of butadienes, catalysts for)

IT Hydrosilylation catalysts  
 (stereoselective, chiral group 10 metal complexes, for butadienes with fluorohydrosilanes)

IT 71307-87-4 76374-09-9  
 RL: CAT (Catalyst use); USES (Uses)  
 (catalyst, for asym. hydrosilylation of butadienes with fluorohydrosilanes)

IT 12012-95-2, Allylchloropalladium dimer 149917-88-4  
 RL: CAT (Catalyst use); USES (Uses)  
 (catalysts contg., for asym. hydrosilylation of butadienes with fluorohydrosilanes)

IT 1631-83-0, Chlorodiphenylsilane 1631-84-1, Dichlorophenyldisilane  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (fluorination of)

IT 542-92-7, Cyclopentadiene, uses 2004-70-8, (E)-1,3-Pentadiene  
 16939-57-4, (E)-1-Phenyl-1,3-butadiene  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (hydrosilylation of, by fluorohydrosilanes, stereoselective, chiral group 10 metal complex catalysts for)

IT 696-35-5P, Difluorophenylsilane 1013-91-8P, Fluorodiphenylsilane  
 RL: SPN (Synthetic preparation); PREP (Preparation)  
 (prepn. and asym. hydrosilylation by, of butadienes, chiral group 10 metal catalysts for)

IT 22135-49-5P, (S)-1-Phenyl-1-butanol 22144-60-1P, (R)-1-Phenyl-1-butanol  
 102339-78-6P, (R)-2-Pentyl benzoate 153841-08-8P, (S)-(Z)-1-Phenyl-1-triphenylsilyl-2-butene 153841-09-9P, (R)-(Z)-4-(Triphenylsilyl)-2-pentene  
 RL: SPN (Synthetic preparation); PREP (Preparation)  
 (prepn. of)

IT 64770-02-1P, 3-(Methyldiphenylsilyl)cyclopentene  
 RL: SPN (Synthetic preparation); PREP (Preparation)  
 (prepn. of optically active)

IT 153841-05-5P, 3-(Fluorodiphenylsilyl)cyclopentene  
 RL: SPN (Synthetic preparation); PREP (Preparation)  
 (prepn. of optically active, as intermediates for allyl alcs.)

IT 153841-03-3P 153841-04-4P, (R)-(Z)-4-(Difluorophenylsilyl)-2-pentene  
 153841-06-6P 153841-07-7P  
 RL: SPN (Synthetic preparation); PREP (Preparation)  
 (prepn. of, as intermediate for chiral allyl alcs.)

IT 153841-02-2P  
 RL: SPN (Synthetic preparation); PREP (Preparation)  
 (prepn. of, catalysts contg., for asym. hydrosilylation of butadienes with fluorohydrosilanes)

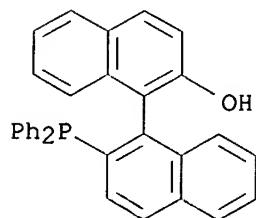
IT 115793-56-1P, (S)-(Z)-1-Phenyl-2-buten-1-ol  
 RL: SPN (Synthetic preparation); PREP (Preparation)  
 (prepn. of, optically active allylfluorosilanes as intermediates for)

IT 18162-48-6  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (silylation by, of hydroxydiphenylphosphinobinaphthyl)

IT 149917-88-4  
 RL: CAT (Catalyst use); USES (Uses)  
 (catalysts contg., for asym. hydrosilylation of butadienes with fluorohydrosilanes)

RN 149917-88-4 HCPLUS

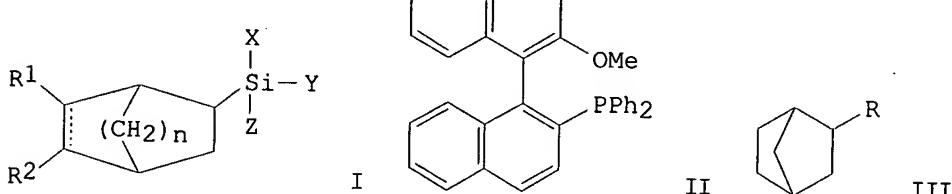
CN [1,1'-Binaphthalen]-2-ol, 2'-(diphenylphosphino)-, (1R)- (9CI) (CA INDEX NAME)



L81 ANSWER 16 OF 18 HCPLUS COPYRIGHT 2003 ACS  
 AN 1994:218160 HCPLUS  
 DN 120:218160  
 TI Preparation of optically active silylbicycloalkane or -alkene compounds  
 IN Hayashi, Tamio; Uozumi, Yasuhiro  
 PA Kanegafuchi Chemical Ind, Japan  
 SO Jpn. Kokai Tokyo Koho, 6 pp.  
 CODEN: JKXXAF

DT Patent  
 LA Japanese  
 IC ICM C07F007-08  
 ICS C07F007-10; C07F007-14; C07F007-18  
 CC 29-6 (Organometallic and Organometalloidal Compounds)  
 FAN.CNT 1

|      | PATENT NO.        | KIND | DATE         | APPLICATION NO. | DATE         |
|------|-------------------|------|--------------|-----------------|--------------|
| PI   | JP 05255351       | A2   | 19931005     | JP 1992-51389   | 19920310 <-- |
|      | JP 3279620        | B2   | 20020430     |                 |              |
| PRAI | JP 1992-51389     |      | 19920310 <-- |                 |              |
| OS   | MARPAT 120:218160 |      |              |                 |              |
| GI   |                   |      |              |                 |              |



AB The title compds. [I; R1, R2 = H, alkyl, aralkyl, aryl, alkoxy carbonyl, cyano, NO<sub>2</sub>; X, Y, Z = H, alkyl, alkoxy, halo; n = 1, 2; dotted line = unsatd. or satd.] are prep'd. by asym. hydrosilylation of unsatd. bicyclic compds. in the presence of chiral phosphine catalysts. A mixt. of norbornene, HSiCl<sub>3</sub>, allylpalladium chloride dimer, and (R)-(+)-II was stirred under cooling, then heated at 100.degree. to give 95.5% (1S, 2S, 4R)-II (R = SiCl<sub>3</sub>), which was treated with EtOH and Et<sub>3</sub>N in Et<sub>2</sub>O at room temp. to give 86% (1S, 2S, 4R)-III [R = Si(OEt)<sub>3</sub>]. Hydroxylation of the silyl ether with KHCO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> in MeOH/THF at 50.degree. gave 72% exo-norborneol.

ST chiral silylbicycloalkane; asym hydrosilylation norbornene bicyclooctene  
 IT Hydrosilylation  
 (asym., of norbornene and bicyclooctene derivs.)

IT 121-46-0, Norbornadiene 498-66-8, Norbornene 931-64-6,  
 Bicyclo[2.2.2]octene  
 RL: RCT (Reactant); RACT (Reactant or reagent)

(asym. hydrosilylation of, chiral catalysts for)

IT 145964-33-6

RL: CAT (Catalyst use); USES (Uses)  
 (catalyst, for asym. hydrosilylation of norbornene)

IT 146075-48-1P

RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)  
 (prepn. and ethoxylation of)

IT 153924-15-3P

RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)  
 (prepn. and hydrolysis of)

IT 280-33-1P, Bicyclo[2.2.2]octane 497-37-0P 2890-98-4P,  
 exo-5-Hydroxy-2-norbornene 65118-94-7P

RL: SPN (Synthetic preparation); PREP (Preparation)  
 (prepn. of)

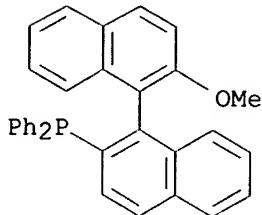
IT 145964-33-6

RL: CAT (Catalyst use); USES (Uses)  
 (catalyst, for asym. hydrosilylation of norbornene)

RN 145964-33-6 HCPLUS

CN Phosphine, [(1R)-2'-methoxy[1,1'-binaphthalen]-2-yl]diphenyl- (9CI) (CA)

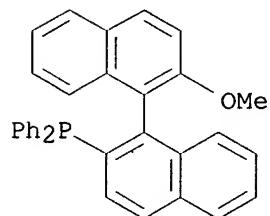
INDEX NAME)



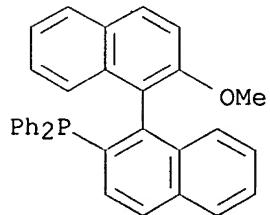
L81 ANSWER 17 OF 18 HCPLUS COPYRIGHT 2003 ACS  
 AN 1994:133865 HCPLUS  
 DN 120:133865  
 TI Preparation of optically active 1-alkenes as intermediates for terpenes  
 IN Hayashi, Tamio; Matsumoto, Yonetatsu; Naito, Masaki  
 PA Kuraray Co, Japan  
 SO Jpn. Kokai Tokkyo Koho, 7 pp.  
 CODEN: JKXXAF  
 DT Patent  
 LA Japanese  
 IC ICM C07C011-12  
 ICS B01J031-04; B01J031-24; C07C001-213; C07C001-30; C07C011-02  
 ICA C07B061-00  
 CC 23-17 (Aliphatic Compounds)  
 Section cross-reference(s): 30  
 FAN.CNT 1

|      | PATENT NO.   | KIND | DATE         | APPLICATION NO. | DATE         |
|------|--|------|--------------|-----------------|--------------|
| PI   | JP 05238964  | A2   | 19930917     | JP 1992-76311   | 19920227 <-- |
|      | JP 3120409   | B2   | 20001225     |                 |              |
| PRAI | JP 1992-76311  |      | 19920227 <-- |                 |              |
| OS   | CASREACT 120:133865; MARPAT 120:133865   |      |              |                 |              |
| AB   | R1R2CHCH:CH <sub>2</sub> [R <sub>1</sub> , R <sub>2</sub> = (un)substituted alkyl, (un)substituted alkenyl, (un)substituted aryl; R <sub>1</sub> ≠ R <sub>2</sub> ] are prep'd. by asym. redn. of R1R2C:CHCH <sub>2</sub> X (R <sub>1</sub> , R <sub>2</sub> = same as above; X = leaving group) in the presence of Pd compds., optically active phosphines, tertiary amines, and HCO <sub>2</sub> H. Geranyl acetate was treated with tris(dibenzylideneacetone)dipalladium-chloroform, (S)-2-diphenylphosphino-2'-methoxy-1,1'-binaphthyl, Et <sub>3</sub> N, and HCO <sub>2</sub> H in THF at 40.degree. for 4 h to give 94% (R)-3,7-dimethyl-1,6-octadiene (55% ee). |      |              |                 |              |
| ST   | optically active alkene intermediate terpene; asym redn unsatd acetate; palladium phosphine additive asym redn; tertiary amine formate asym redn   |      |              |                 |              |
| IT   | Terpenes and Terpenoids, preparation   |      |              |                 |              |
|      | RL: PREP (Preparation)<br>(intermediates for, optically active alkenes as)   |      |              |                 |              |
| IT   | Reduction<br>(stereoselective, of unsatd. acetates, in prepn. of optically active alkenes as intermediates for terpenes)   |      |              |                 |              |
| IT   | Amines, uses<br>RL: USES (Uses)<br>(tertiary, in asym. redn. of unsatd. acetates)  |      |              |                 |              |
| IT   | Alkenes, preparation<br>RL: SPN (Synthetic preparation); PREP (Preparation)<br>(.alpha.-, prepn. of, optically active, as intermediates for terpenes)  |      |              |                 |              |
| IT   | 62-53-3, Aniline, reactions<br>RL: RCT (Reactant); RACT (Reactant or reagent)<br>(amidation of, with dicarboxylic acid)  |      |              |                 |              |
| IT   | 105-87-3, Geranyl acetate 141-12-8, Neryl acetate<br>RL: RCT (Reactant); RACT (Reactant or reagent)  |      |              |                 |              |

(asym. redn. of)  
IT 64-18-6, Formic acid, uses 121-44-8, Triethylamine, uses  
RL: USES (Uses)  
(in asym. redn. of unsatd. acetates)  
IT 51364-51-3, Tris(dibenzylideneacetone)dipalladium 134484-36-9,  
(S)-(-)-2-Diphenylphosphino-2'-methoxy-1,1'-binaphthyl 145964-33-6  
, (R)-(+)-2-Diphenylphosphino-2'-methoxy-1,1'-binaphthyl  
RL: RCT (Reactant); RACT (Reactant or reagent)  
(in asym. redn. of unsatd. acetates)  
IT 1115-82-8P 153279-32-4P  
RL: SPN (Synthetic preparation); PREP (Preparation)  
(prepn. of)  
IT 10281-55-7P, (S)-3,7-Dimethyl-1,6-octadiene 10281-56-8P,  
(R)-3,7-Dimethyl-1,6-octadiene  
RL: SPN (Synthetic preparation); PREP (Preparation)  
(prepn. of, from unsatd. acetate, as intermediate for terpenes)  
IT 134484-36-9, (S)-(-)-2-Diphenylphosphino-2'-methoxy-1,1'-  
binaphthyl 145964-33-6, (R)-(+)-2-Diphenylphosphino-2'-methoxy-  
1,1'-binaphthyl  
RL: RCT (Reactant); RACT (Reactant or reagent)  
(in asym. redn. of unsatd. acetates)  
RN 134484-36-9 HCPLUS  
CN Phosphine, [(1S)-2'-methoxy[1,1'-binaphthalen]-2-yl]diphenyl- (9CI) (CA  
INDEX NAME)



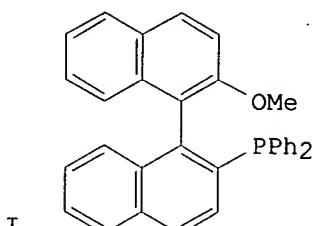
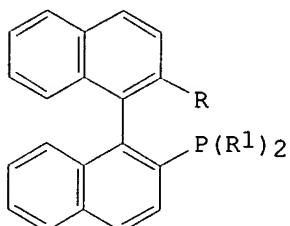
RN 145964-33-6 HCPLUS  
CN Phosphine, [(1R)-2'-methoxy[1,1'-binaphthalen]-2-yl]diphenyl- (9CI) (CA  
INDEX NAME)



L81 ANSWER 18 OF 18 HCPLUS COPYRIGHT 2003 ACS  
AN 1993:7190 HCPLUS  
DN 118:7190  
TI Preparation of optically active binaphthylphosphines as components of  
enantioselective hydrosilylation catalysts  
IN Hayashi, Tamio; Uozumi, Yasuhiro; Yamazaki, Akiko; Kumobayashi, Hidenori  
PA Takasago International Corp., Japan  
SO Eur. Pat. Appl., 12 pp.  
CODEN: EPXXDW  
DT Patent  
LA English

IC ICM C07F009-50  
 ICS C07F015-00; B01J031-28  
 CC 29-7 (Organometallic and Organometalloidal Compounds)  
 FAN.CNT 1

|      | PATENT NO.                    | KIND | DATE         | APPLICATION NO. | DATE         |
|------|-------------------------------|------|--------------|-----------------|--------------|
| PI   | EP 503884                     | A1   | 19920916     | EP 1992-302010  | 19920310 <-- |
|      | EP 503884                     | B1   | 19950726     |                 |              |
|      | R: CH, DE, FR, GB, IT, LI, NL |      |              |                 |              |
|      | JP 05017491                   | A2   | 19930126     | JP 1991-266864  | 19910919 <-- |
|      | JP 2733880                    | B2   | 19980330     |                 |              |
|      | US 5231202                    | A    | 19930727     | US 1992-850998  | 19920312 <-- |
| PRAI | JP 1991-70339                 |      | 19910312 <-- |                 |              |
|      | JP 1991-266864                |      | 19910919 <-- |                 |              |
| OS   | MARPAT 118:7190               |      |              |                 |              |
| GI   |                               |      |              |                 |              |



I II

AB Title compds. [I; R = alkyl, OR2; R1 = Ph, pentafluorophenyl; R2 = H, cycloalkyl, (halo)alkyl, (alkoxy)alkoxy, Ph], were prep'd. Thus, (S)-2,2'-binaphthol was stirred with (F3CSO2)2 and pyridine in CH2Cl2 overnight to give 92% bis-triflate which was stirred with Ph2P(O)H, Pd(OAc)2, and 1,4-bis(diphenylphosphino)butane in Me2SO at 100.degree. for 12 h to give 96% (S)-(-)-2-trifluoromethanesulfonyl-2'-diphenylphosphinoyl-1,1'-binaphthyl. The latter was hydrolyzed with 3N NaOH in MeOH/dioxane in 81.5% yield and the product was O-methylated with MeI/K2CCO3/acetone (98%) and reduced with Cl3SiH/Et3N in xylene (79%) to give 19% (S)-II. This was used to enantioselectively hydrosilylate 1-phenyl-1,3-butadiene with Cl3SiH.

ST binaphthylphosphine alkoxy prepn hydrosilylation catalyst  
 IT Hydrosilylation catalysts  
     (binaphthylphosphines)  
 IT Hydrosilylation  
     (by trichlorosilane)  
 IT 925-90-6, Ethylmagnesium bromide  
     RL: RCT (Reactant); RACT (Reactant or reagent)  
       (Grignard reaction of, with triflyloxydiphenylphosphinoylbinaphthyl)  
 IT 75-30-9, Isopropyl iodide  
     RL: RCT (Reactant); RACT (Reactant or reagent)  
       (alkylation by, of hydroxydiphenylphosphinoylbinaphthyl)  
 IT 100-39-0, Benzylbromide  
     RL: RCT (Reactant); RACT (Reactant or reagent)  
       (benzylation by, of hydroxydiphenylphosphinoylbinaphthyl)  
 IT 18531-99-2  
     RL: PROC (Process)  
       (conversion of, to triflate diester, in prepn. of enantioselective  
       hydrosilylation catalyst)  
 IT 1515-78-2, 1-Phenyl-1,3-butadiene  
     RL: RCT (Reactant); RACT (Reactant or reagent)  
       (enantioselective hydrosilylation of, naphthylphosphine catalysts for)  
 IT 10025-78-2, Trichlorosilane  
     RL: RCT (Reactant); RACT (Reactant or reagent)

(hydrosilylation by, of phenylbutadiene, enantioselective by naphthylphosphinehydrosilylation catalysts for)

IT 3347-57-7P 81176-43-4P 144868-13-3P 144868-14-4P  
RL: SPN (Synthetic preparation); PREP (Preparation)  
(prepn. of)

IT 134484-36-9P 137769-31-4P 144868-17-7P  
RL: SPN (Synthetic preparation); PREP (Preparation)  
(prepn. of, as enantioselective hydrosilylation catalyst)

IT 137769-30-3P 144868-15-5P  
RL: SPN (Synthetic preparation); PREP (Preparation)  
(prepn. of, as enantioselective hydrosilylation catalyst)

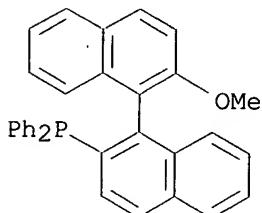
IT 137769-28-9P 144868-16-6P  
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IT 128544-05-8P 134484-37-0P 137769-27-8P 137769-33-6P 137769-34-7P  
RL: SPN (Synthetic preparation); PREP (Preparation)  
(prepn. of, as intermediate for enantioselective hydrosilylation catalysts)

IT 134484-36-9P  
RL: SPN (Synthetic preparation); PREP (Preparation)  
(prepn. of, as enantioselective hydrosilylation catalyst)

RN 134484-36-9 HCPLUS

CN Phosphine, [(1S)-2'-methoxy[1,1'-binaphthalen]-2-yl]diphenyl- (9CI) (CA INDEX NAME)



=> fil reg

FILE 'REGISTRY' ENTERED AT 10:00:04 ON 12 MAY 2003  
USE IS SUBJECT TO THE TERMS OF YOUR STN CUSTOMER AGREEMENT.  
PLEASE SEE "HELP USAGETERMS" FOR DETAILS.  
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STRUCTURE FILE UPDATES: 11 MAY 2003 HIGHEST RN 514167-89-6  
DICTIONARY FILE UPDATES: 11 MAY 2003 HIGHEST RN 514167-89-6

TSCA INFORMATION NOW CURRENT THROUGH JANUARY 6, 2003

Please note that search-term pricing does apply when conducting SmartSELECT searches.

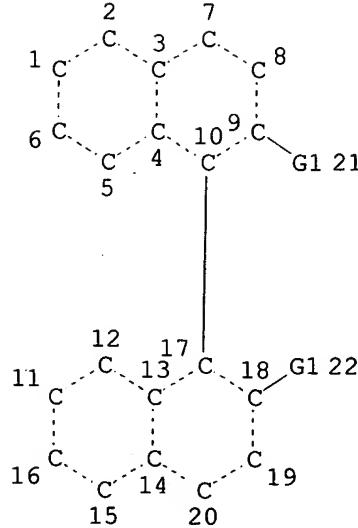
Crossover limits have been increased. See HELP CROSSOVER for details.

Experimental and calculated property data are now available. See HELP PROPERTIES for more information. See STNote 27, Searching Properties in the CAS Registry File, for complete details:  
<http://www.cas.org/ONLINE/STN/STNOTES/stnotes27.pdf>

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L11 3 SEA FILE=REGISTRY ABB=ON PLU=ON L10 AND C34H40NP  
 L19 STR



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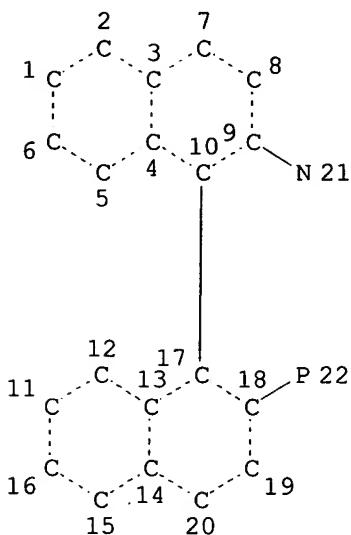
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NUMBER OF NODES IS 22

STEREO ATTRIBUTES: NONE

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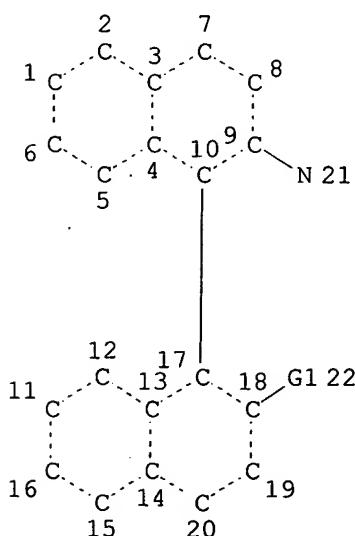
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L48 75 SEA FILE=REGISTRY SUB=L22 SSS FUL L46  
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VAR G1=AS/O/S

NODE ATTRIBUTES:

DEFAULT MLEVEL IS ATOM  
 DEFAULT ECLEVEL IS LIMITED

GRAPH ATTRIBUTES:

RING(S) ARE ISOLATED OR EMBEDDED  
NUMBER OF NODES IS 22

STEREO ATTRIBUTES: NONE

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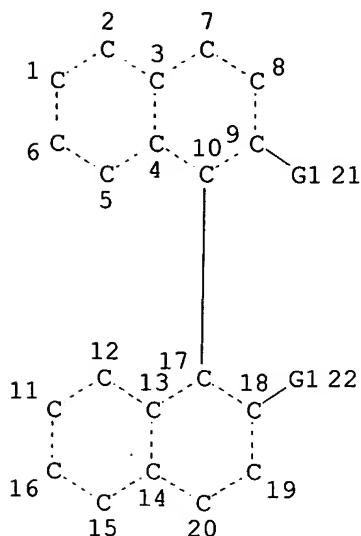
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169 ANSWERS

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L11 3 SEA FILE=REGISTRY ABB=ON PLU=ON L10 AND C34H40NP  
L19 STR



VAR G1=N/P/AS/O/S

NODE ATTRIBUTES:

DEFAULT MLEVEL IS ATOM

DEFAULT ECLEVEL IS LIMITED

GRAPH ATTRIBUTES:

RING(S) ARE ISOLATED OR EMBEDDED

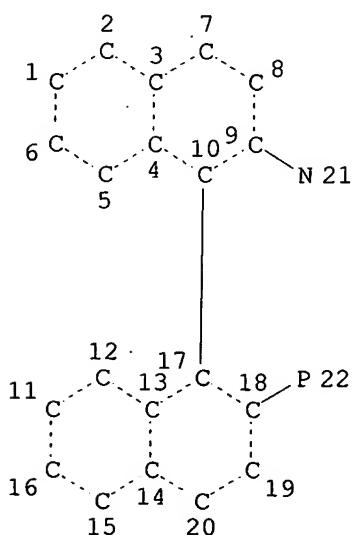
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STEREO ATTRIBUTES: NONE

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L46 STR



NODE ATTRIBUTES:

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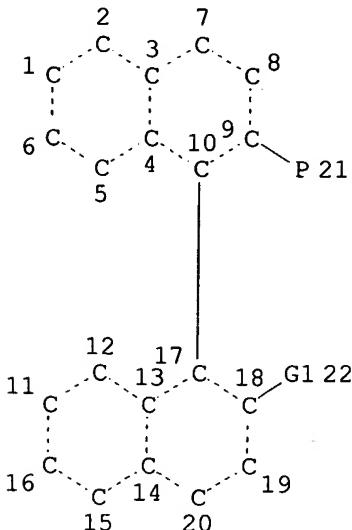
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STEREO ATTRIBUTES: NONE

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VAR G1=AS/O/S

NODE ATTRIBUTES:

DEFAULT MLEVEL IS ATOM

DEFAULT ECLEVEL IS LIMITED

GRAPH ATTRIBUTES:

RING(S) ARE ISOLATED OR EMBEDDED

NUMBER OF NODES IS 22

STEREO ATTRIBUTES: NONE

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257 ANSWERS

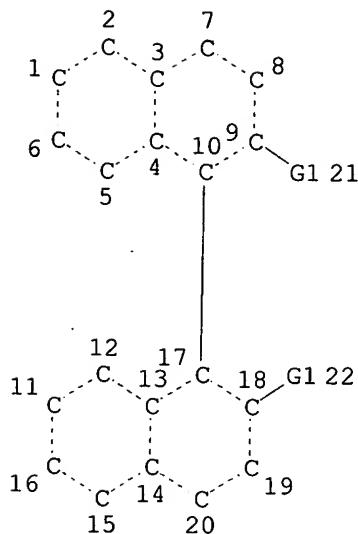
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DEFAULT ECLEVEL IS LIMITED

GRAPH ATTRIBUTES:

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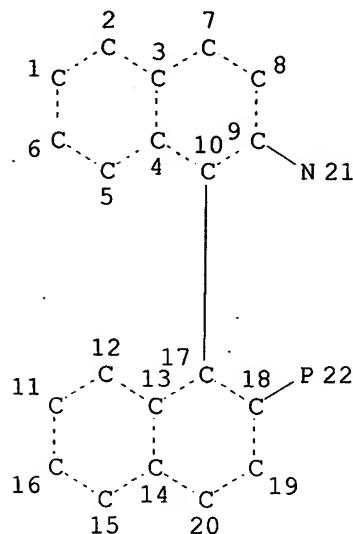
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STEREO ATTRIBUTES: NONE

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L46                 STR



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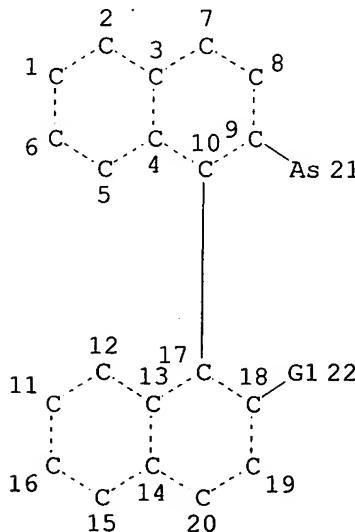
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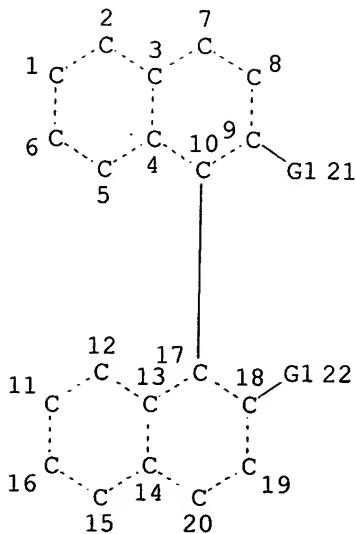
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0 ANSWERS

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 /BI OR 2920-38-9/BI OR 2928-43-0/BI OR 31144-33-9/BI OR  
 3375-31-3/BI OR 39253-43-5/BI OR 3972-65-4/BI OR 3976-34-9/BI  
 OR 39910-98-0/BI OR 40138-16-7/BI OR 402-43-7/BI OR 4075-79-0/B  
 I OR 42371-64-2/BI OR 460-00-4/BI OR 4688-76-0/BI OR 51364-51-3  
 /BI OR 534-17-8/BI OR 53847-33-9/BI OR 54000-83-8/BI OR  
 5405-15-2/BI OR 54660-04-7/BI OR 553-94-6/BI OR 556-96-7/BI OR  
 563-80-4/BI OR 565-69-5/BI OR 5720-06-9/BI OR 576-22-7/BI OR  
 583-53-9/BI OR 583-55-1/BI OR 592-41-6/BI OR 59734-92-8/BI OR  
 613-37-6/BI OR 619-42-1/BI OR 623-03-0/BI OR 623-12-1/BI OR  
 626-60-8/BI OR 644-08-6/BI OR 6476-37-5

L11 3 SEA FILE=REGISTRY ABB=ON PLU=ON L10 AND C34H40NP  
 L19 STR



VAR G1=N/P/AS/O/S

NODE ATTRIBUTES:

DEFAULT MLEVEL IS ATOM

DEFAULT ECLEVEL IS LIMITED

GRAPH ATTRIBUTES:

RING(S) ARE ISOLATED OR EMBEDDED

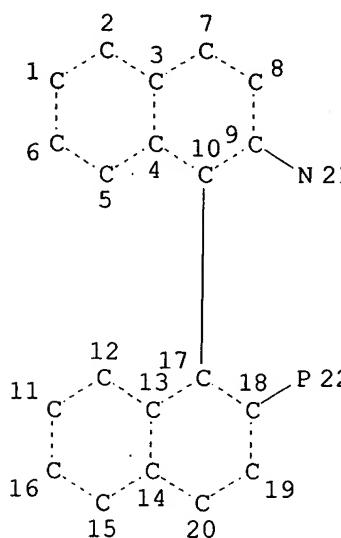
NUMBER OF NODES IS 22

STEREO ATTRIBUTES: NONE

L21 6721 SEA FILE=REGISTRY SSS FUL L19

L22 6718 SEA FILE=REGISTRY ABB=ON PLU=ON L21 NOT L11

L46 STR



NODE ATTRIBUTES:

DEFAULT MLEVEL IS ATOM

DEFAULT ECLEVEL IS LIMITED

GRAPH ATTRIBUTES:

RING(S) ARE ISOLATED OR EMBEDDED

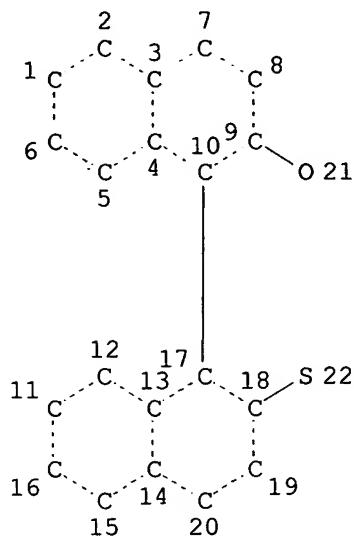
NUMBER OF NODES IS 22

STEREO ATTRIBUTES: NONE

L48 75 SEA FILE=REGISTRY SUB=L22 SSS FUL L46

L54 6643 SEA FILE=REGISTRY ABB=ON PLU=ON L22 NOT L48

L61 STR



## NODE ATTRIBUTES:

DEFAULT MLEVEL IS ATOM  
 DEFAULT ECLEVEL IS LIMITED

## GRAPH ATTRIBUTES:

RING(S) ARE ISOLATED OR EMBEDDED  
 NUMBER OF NODES IS 22

## STEREO ATTRIBUTES: NONE

L62 56 SEA FILE=REGISTRY SUB=L54 SSS FUL L61

100.0% PROCESSED 276 ITERATIONS  
 SEARCH TIME: 00.00.01

56 ANSWERS

=> d his

(FILE 'HOME' ENTERED AT 08:44:27 ON 12 MAY 2003)  
 SET COST OFF

FILE 'HCAPLUS' ENTERED AT 08:44:46 ON 12 MAY 2003

E BUCHWALD S/AU

L1 296 S E3,E4,E6-E9

E OLD D/AU

L2 15 S E3,E5,E7,E8

E WOLFE J/AU

L3 201 S E3,E17,E18

E WOLFE JOHN/AU

L4 38 S E3,E11,E12

E PALUCKI M/AU

L5 26 S E3,E4

E KAMIKAWA K/AU

L6 22 S E3,E8

L7 5 S E9-E12

L8 2 S (US20020156295 OR US6307087 OR US6395916)/PN OR WO99-US15450/

L9 2 S L1-L7 AND L8

SEL RN

FILE 'REGISTRY' ENTERED AT 08:47:36 ON 12 MAY 2003

L10 486 S E1-E486

L11           3 S L10 AND C34H40NP  
        SEL RN  
L12           0 S E487-E489/CRN

FILE 'HCAOLD' ENTERED AT 08:50:52 ON 12 MAY 2003  
L13           0 S L11

FILE 'HCAPLUS' ENTERED AT 08:50:58 ON 12 MAY 2003  
L14           7 S L11  
L15           6 S L14 AND L1-L9  
L16           1 S L14 NOT L15  
L17           7 S L15,L16

FILE 'USPATFULL, USPAT2' ENTERED AT 08:51:23 ON 12 MAY 2003  
L18           3 S L11

FILE 'REGISTRY' ENTERED AT 08:52:42 ON 12 MAY 2003

FILE 'USPATFULL, USPAT2' ENTERED AT 08:52:53 ON 12 MAY 2003

FILE 'HCAPLUS' ENTERED AT 08:53:44 ON 12 MAY 2003

FILE 'REGISTRY' ENTERED AT 08:54:49 ON 12 MAY 2003  
L19           STR  
L20           50 S L19  
L21           6721 S L19 FUL  
             SAV TEMP L21 SACKEY004/A  
L22           6718 S L21 NOT L11  
L23           7 S L22 AND L10  
L24           5728 S L22 NOT (PMS OR CCS OR MNS)/CI

FILE 'HCAPLUS' ENTERED AT 08:59:36 ON 12 MAY 2003  
L25           4102 S L22  
L26           44 S L1-L9 AND L25  
             SEL HIT RN

FILE 'REGISTRY' ENTERED AT 09:00:08 ON 12 MAY 2003  
L27           50 S E490-E539

FILE 'HCAPLUS' ENTERED AT 09:01:02 ON 12 MAY 2003  
L28           2247 S L27  
L29           44 S L26 AND L28  
L30           22 S L29 AND (PY<=1998 OR PRY<=1998 OR AY<=1998)  
L31           7 S L30 AND ORGANOMETAL?/SC,SX  
L32           35 S L27 (L) CAT/RL AND L29  
L33           15 S L30 AND L32  
L34           19 S L31,L33

FILE 'REGISTRY' ENTERED AT 09:03:53 ON 12 MAY 2003

FILE 'HCAPLUS' ENTERED AT 09:04:07 ON 12 MAY 2003  
L35           3 S L30 NOT L34  
L36           3933 S L24,L28 NOT L17,L26,L29-L35  
L37           2375 S L36 AND (PY<=1998 OR PRY<=1998 OR AY<=1998)  
L38           365 S L37 AND ORGANOMETAL?/SC,SX  
L39           1358 S L25(L)CAT/RL  
L40           895 S L28(L)CAT/RL  
L41           578 S L37 AND L39,L40  
L42           116 S L38 AND L41  
L43           516 S L37 AND LIGAND  
L44           69 S L43 AND L42  
             SEL HIT RN

FILE 'REGISTRY' ENTERED AT 09:36:26 ON 12 MAY 2003

L45        230 S E540-E770  
L46        STR L19  
L47        2 S L46 SAM SUB=L22  
L48        75 S L46 FUL SUB=L22  
            SAV L48 SACKEY004A/A

FILE 'HCAPLUS' ENTERED AT 09:39:41 ON 12 MAY 2003

L49        30 S L48  
L50        7 S L49 AND (PY<=1998 OR PRY<=1998 OR AY<=1998)  
L51        5 S L50 NOT L29-L34  
L52        2 S L51 AND (PD<=19980710 OR PRD<=19980710 OR AD<=19980710)

FILE 'REGISTRY' ENTERED AT 09:41:46 ON 12 MAY 2003

FILE 'HCAPLUS' ENTERED AT 09:41:53 ON 12 MAY 2003

FILE 'REGISTRY' ENTERED AT 09:42:30 ON 12 MAY 2003

L53        STR L19  
L54        6643 S L22 NOT L48  
L55        3 S L53 SAM SUB=L54  
L56        169 S L53 FUL SUB=L54  
            SAV L56 SACKEY044B/A  
L57        STR L53  
L58        257 S L57 FUL SUB=L54  
            DEL SACKEY044B/A  
            SAV L56 SACKEY004B/A  
            SAV L58 SACKEY004C/A  
L59        STR L57  
L60        0 S L59 FUL SUB=L54  
            SAV L60 SACKEY004D/A  
L61        STR L59  
L62        56 S L61 FUL SUB=L54  
            SAV L62 SACKEY004E/A

FILE 'HCAPLUS' ENTERED AT 09:46:41 ON 12 MAY 2003

L63        243 S L56 OR L58 OR L62  
L64        138 S L63 AND (PD<=19980710 OR PRD<=19980710 OR AD<=19980710)  
L65        70 S L64 AND LIGAND  
L66        57 S L64 AND ORGANOMETAL?/SC, SX  
L67        146 S L63 (L) CAT/RL  
L68        132 S L63 (L) (RACT OR RCT OR RGT)/RL  
L69        124 S L64 AND L67, L68  
L70        86 S L65, L66 AND L69  
L71        63 S L70 NOT P/DT  
L72        23 S L70 NOT L71  
            SEL HIT RN

FILE 'REGISTRY' ENTERED AT 09:49:05 ON 12 MAY 2003

L73        79 S E771-E849  
L74        7 S L73 AND (C32H22BROP OR C33H25OP OR C33H23CL2OP OR C36H31OP OR  
L75        14 S L73 AND (C33H25O2P OR C32H22BRO2P OR C35H29OP OR C41H29O2P OR  
L76        11 S L75 NOT L74  
            SEL RN 1 4 5 8  
L77        4 S E850-E853

FILE 'HCAPLUS' ENTERED AT 09:58:25 ON 12 MAY 2003

L78        93 S L74 OR L77  
L79        16 S L78 AND L72  
L80        60 S L78 AND (PD<=19980710 OR PRD<=19980710 OR AD<=19980710)  
L81        18 S L80 AND P/DT

FILE 'HCAPLUS' ENTERED AT 09:59:44 ON 12 MAY 2003

sackey - 10 / 004101

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FILE 'REGISTRY' ENTERED AT 10:00:04 ON 12 MAY 2003